

Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
(Rev. 5-93)TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO

M 6820 PCT/US

U.S. APPLICATION NO. (if known, sec. 17, CFR 1.5)

09/807658

INTERNATIONAL APPLICATION NO

PCT/JP99/05652

INTERNATIONAL FILING DATE

October 14, 1999

PRIORITY DATE CLAIMED

10/15/1998 and 10/08/1999

TITLE OF INVENTION

HYDROPHILIZING AGENT FOR METALLIC MATERIAL, HYDROPHILIZING FLUID, METHOD OF
HYDROPHILIZING, METALLIC MATERIAL, AND HEAT EXCHANGER

APPLICANT(S) FOR DO/EO/US

Kazuya Nakada and Takuo Murai

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371
 2. ☐ This a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1)
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2))
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☐ have been transmitted by the International Bureau
 - c. ☐ have not been made, however, the time limit for making such amendments has NOT expired
 - d. ☒ have not been made and will not be made
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unexecuted)
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))
- Items 11. to 16. below concern other document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98
 12. ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
 13. ☒ A FIRST preliminary amendment
 ☐ A SECOND or SUBSEQUENT preliminary amendment.
 14. ☐ A substitute specification
 15. ☐ A change of power of attorney and/or address letter
 16. ☐ Other items or information .

"Express Mail" mailing label number EL615776137US

U.S. Application No. (If known see CFR 1.30) <div style="font-size: 1.5em; font-weight: bold; margin-left: 100px;">09/ 807658</div>	INTERNATIONAL APPLICATION NO. PCT/JP99/05652	ATTORNEY'S DOCKET NUMBER M 6820 PCT/US
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17. ■ The following fees are submitted.

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO..... **\$860.00**

International preliminary examination fee paid to USPTO (37CFR 1.482)..... **\$670.00**

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2))..... **\$690.00**

Neither international preliminary examination fee (37CFR 1.482) nor international search fee(37 CFR 1.445(a)(2)) paid toUSPTO.. **\$970.00**

International preliminary examination fee paid to USPTO (37CFR 1.482)and all claims satisfied provisions of PCT Article 33(2)-(4)..... **\$96.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS	PTO USE ONLY
\$ 860	00
\$ 0	00
\$ 0	00
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Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e))					
Claims	Number filed	Number Extra	Rate		
Total Claims	1 - 20 =	0	0 X \$18.00	\$ 0	00
Independent Claims	1 - 3 =	0	0 X \$78.00	\$ 0	00
Multiple dependent claims (s)(if applicable) 0			+ \$260.00	\$ 0	00
TOTAL OF ABOVE CALCULATIONS =				\$ 860	00
Reduction by ½ for filing by small entity, if applicable Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)				\$ 0	00
SUBTOTAL =				\$ 860	00
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f))				\$ 0	00
TOTAL NATIONAL FEE =				\$ 860	00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property				\$ 0	00
TOTAL FEES ENCLOSED =				\$ 860	00
				Amount to be refunded	\$-----
				charged	\$860.00

a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed

b. ■ Please charge my Deposit Account No. 01-1250 in the amount of \$860.00 to cover the above fees
A triplicate copy of this sheet is enclosed. Order No. 01-0313.

c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-1250. A triplicate copy of this sheet is enclosed

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept
2500 Renaissance Blvd, Suite 200
Gulph Mills, PA 19406

SIGNATURE

Stephen D. Harper
NAME ATTORNEY FOR APPLICANT
33,243
REGISTRATION NUMBER

09/807658

JC03 Rec'd PCT/PTO 16 APR 2001

"Express Mail" mailing label number EL65-776 B7 US Date of Deposit 4-16-01

PATENT
Docket No. M 6820 HST/NI PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RE: PCT/JP99/05652
International Filing Date: October 8, 1999
Priority Date Claimed: October 15, 1998
October 8, 1999
Applicant: Nakada et al.
Title: HYDROPHILIZING AGENT FOR METALLIC MATERIAL,
HYDROPHILIZING FLUID, METHOD OF HYDROPHILIZING, METALLIC MATERIAL,
AND HEAT EXCHANGER
Applicants' Reference: M 6820 HST/NI PCT/US

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Box PCT
Washington, DC 20231

ATTN: DO/EO/US

Sir:

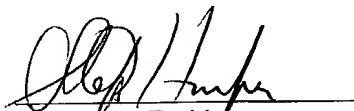
Before examining this application, please enter the following amendment.

IN THE CLAIMS:

Please cancel claims 2-9, without prejudice.

Should any fees be deemed necessary to enter this amendment, please charge them to Deposit Account No. 01-1250.

Respectfully submitted,


Stephen D. Harper
(Reg. No. 33,243)
Attorney for Applicants
(610) 278-4927

Henkel Corporation
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2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

PATENT
Docket No. M 6820 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of Nakada et al.

Serial No. 09/807658
Filed:
Title: HYDROPHILIZATION AGENT FOR METALLIC MATERIAL (As Amended)

Examiner:
Art Unit:

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, DC 20231, on 8-23-01.

8-23-01
Date


Signature of certifier

Mary Lynne Carlisle
Typed or printed name of certifier

**SUPPLEMENTAL PRELIMINARY AMENDMENT AND RESPONSE TO
NOTIFICATION OF A DEFECTIVE RESPONSE**

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to substantive examination of the above-referenced application, please enter the following amendment.

IN THE TITLE AND SPECIFICATION:

Enter the separately attached substitute specification, in which a number of amendments to the title and text of the specification are made. These amendments are being made for the purpose of correcting certain informalities and typographical errors in the application as originally translated from the priority International application. No new matter has been added.

In addition to a "clean" version of the specification as amended, a copy of the specification which is marked up to show the specific changes made is also enclosed herewith.

Also enclosed is a corrected translation of the priority International application, responsive to the Notification of a Defective Response mailed July 27, 2001, wherein it was observed that the claims were not correctly translated in the translation submitted July 16, 2001. A marked-up version of the corrected translation is also enclosed.

IN THE CLAIMS:

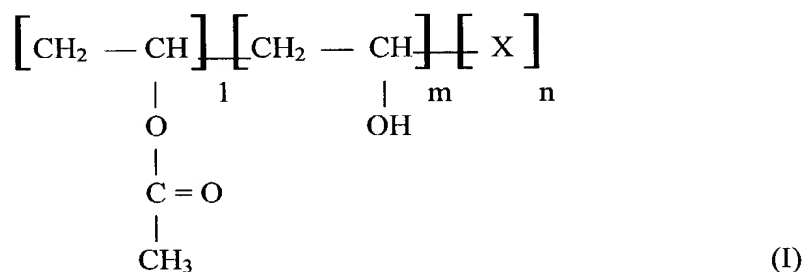
Amend claim 1 to read as follows:

1. (Amended) A hydrophilization agent for metallic material, comprising:
 - (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of primary amide groups, secondary amide groups, tertiary amide groups, hydroxyl groups and polyoxyalkylene groups;
 - (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of sulfonic acid groups, phosphonic acid groups, carboxyl groups, primary amino groups, secondary amino groups, tertiary amino groups, and quaternary ammonium groups;
 - (C) a vanadium compound; and
 - (D) a compound containing at least one element selected from the group consisting of Zr, Ti, and Si.

Enter the following new claims 10-34:

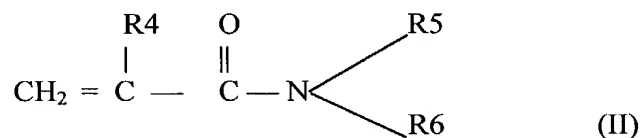
SN 09/807,658

10. (New) A hydrophilization agent according to claim 1 wherein component (A) comprises at least one member selected from the group consisting of polyvinyl alcohol polymers of general formula I



and reaction products of the polyvinyl alcohol polymers of general formula I and diketenes, wherein X is a copolymerizing unit other than vinyl acetate and vinyl alcohol, 1 is the copolymerizing number of moles of a vinyl acetate copolymerizing unit, m is the copolymerizing number of moles of a vinyl alcohol polymerizing unit, and n is the copolymerizing number of moles of copolymerizing unit X, and 1 and n may be zero.

11. (New) A hydrophilization agent according to claim 1, wherein said component (A) comprises at least one acrylamide polymer selected from the group consisting of water-soluble polymers and water-soluble copolymers of an acrylamide compound of general formula II:



wherein R4 is a hydrogen atom or a CH₃ group, and R5 and R6 are, independently of the other, a hydrogen atom, a C1-C4 alkyl group, a benzil group, or a C1-C3 hydroxyalkyl group.

12. (New) A hydrophilization agent according to claim 1, additionally comprising at least one additive selected from the group consisting of water, rust preventives, leveling agents, fillers, coloring agents, water-soluble solvents, anti-bacteria/mildew agents, organic crosslinking agents and surfactants.
13. (New) A hydrophilization agent according to claim 1 comprising:
 - (i) 100 parts by weight component (A);
 - (ii) 0.1 to 1000 parts by weight component (B);
 - (iii) 0.1 to 200 parts by weight component (C); and
 - (iv) 0.1 to 200 parts by weight component (D).
14. (New) A method of treating a surface of a metallic material comprising depositing the hydrophilization agent of claim 1 on said surface and drying the hydrophilization agent deposited on said surface to form a hydrophilic film.
15. (New) A metallic material having a surface with a hydrophilic film thereon, said hydrophilic film being formed by the method of claim 14.
16. (New) The metallic material according to claim 15 wherein said metallic material is a heat exchanger.
17. (New) A hydrophilization agent according to claim 1 comprising:
 - (i) 100 parts by weight component (A);
 - (ii) 1 to 100 parts by weight component (B);
 - (iii) 1 to 100 parts by weight component (C); and

- (iv) 1 to 100 parts by weight component (D).
18. (New) A hydrophilization agent according to claim 1 comprising solvent and:
- (i) 0.05 to 50 g/L of component (A);
 - (ii) 0.05 to 50 g/L of component (B);
 - (iii) 0.05 to 10 g/L of component (C); and
 - (iv) 0.05 to 10 g/L of component (D).
19. (New) A hydrophilization agent according to claim 1 comprising water and:
- (i) 0.5 to 10 g/L of component (A);
 - (ii) 0.5 to 10 g/L of component (B);
 - (iii) 0.5 to 5 g/L of component (C); and
 - (iv) 0.5 to 5 g/L of component (D).
20. (New) A hydrophilization agent in accordance with claim 10 wherein component (A) comprises at least one polyvinyl alcohol polymer of general formula I wherein copolymerizing unit X has a copolymerizing mole ratio $n/1+m+n$ from 0 to 0.4.
21. (New) A hydrophilization agent in accordance with claim 10 wherein component (A) comprises at least one polyvinyl alcohol polymer of general formula I wherein the vinyl acetate polymerizing unit has a copolymerizing mole ratio $1/1+m+n$ from 0 to 0.2.
22. (New) A hydrophilization agent in accordance with claim 11 wherein component (B) comprises at least one acrylamide polymer which does not have a cationic group but which does have at least one ionic functional group selected from the

group consisting of sulfonic acid groups, phosphonic acid groups, and carboxyl groups.

23. (New) A hydrophilization agent in accordance with claim 11 wherein component (B) comprises at least one acrylamide polymer which does not have an anionic group but which does have at least one member selected from the group consisting of primary amino groups, secondary amino groups, tertiary amino groups and quaternary ammonium groups.
24. (New) A hydrophilization agent in accordance with claim 1 wherein component (D) is water-soluble or water-dispersible.
25. (New) A hydrophilization agent obtained by combining with a solvent the following components:
- (A) a hydrophilic polymer having at least one functional group selected from the group consisting of primary amide groups, secondary amide groups, tertiary amide groups, hydroxyl groups and polyoxyalkylene groups;
 - (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of sulfonic acid groups, phosphonic acid groups, carboxyl groups, primary amino groups, secondary amino groups, tertiary amino groups and quaternary ammonium groups;
 - (C) a vanadium compound; and
 - (D) a compound containing at least one element selected from the group consisting of Zr, Ti and Si.
26. (New) A hydrophilization agent in accordance with claim 25 wherein said solvent comprises water.

27. (New) A hydrophilization agent in accordance with claim 25 comprising:
 - (i) 0.05 to 50 g/L of component (A);
 - (ii) 0.05 to 50 g/L of component (B);
 - (iii) 0.05 to 10 g/L of component (C); and
 - (iv) 0.05 to 10 g/L of component (D).
28. (New) A method in accordance with claim 14 wherein said surface is degreased prior to said depositing.
29. (New) A method in accordance with claim 14 wherein said surface is pre-treated by chemical conversion prior to said depositing.
30. (New) A method in accordance with claim 14 wherein said hydrophilic film has a thickness of from 0.05 μm to 5 μm .
31. (New) A metallic material having a surface with a hydrophilic film thereon, said hydrophilic film comprising:
 - (A) a hydrophilic polymer having at least one functional group selected from the group consisting of primary amide groups, secondary amide groups, tertiary amide groups, hydroxyl groups and polyoxyalkylene groups;
 - (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of sulfonic acid groups, phosphonic acid groups, carboxyl groups, primary amino groups, secondary amino groups, tertiary amino groups and quaternary ammonium groups;
 - (C) a vanadium compound; and
 - (D) a compound containing at least one element selected from the group consisting of Zr, Ti and Si.

32. (New) A metallic material in accordance with claim 31, wherein said metallic material is a heat exchanger.
33. (New) A metallic material in accordance with claim 31, wherein said film has a thickness of from 0.05 μm to 5 μm .
34. (New) A metallic material in accordance with claim 31, wherein said film comprises:
- (i) 100 parts by weight of component (A);
 - (ii) 0.1 to 1000 parts by weight of component (B);
 - (iii) 0.1 to 200 parts by weight of component (C); and
 - (iv) 0.1 to 200 parts by weight of component (D).

REMARKS

Claims 1 and 10-34 are now pending in the application, claims 2-9 having been earlier canceled. The amendments to claim 1 are shown in the separately attached substitute specification entitled "Version Marked to Show Changes Made."

Respectfully submitted,



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SUBSTITUTE SPECIFICATION FOR U.S. SER. NO. 09/807658

Hydrophilization Agent for Metallic Material

- 5 This application claims priority from Japanese applications 10/293656, filed 15 October 1998, and 11/288204, filed 8 October 1999, and International application PCT/JP00/05652, filed 8 October 1999.

Field of the Invention

- 10 The present invention relates to a hydrophilization agent, a hydrophilization liquid and a hydrophilization method of metallic material, a metallic material and a heat exchanger. More particularly, the present invention relates to a hydrophilization agent, a hydrophilization liquid free of chromium, which can impart improved hydrophilic property and corrosion resistance to the metallic
15 material, for example the aluminum-based metallic material used for the fins of a heat exchanger. The present invention relates to such metallic material and heat exchanger.

Discussion of the Related Art

- 20 Heretofore, heat exchangers are manufactured by bonding, e, g., brazing, the metallic material, e.g., an aluminum-based metallic material. Most of such heat exchangers are so designed that their heat dissipating and cooling portions have surface area as large as possible to enhance the heat dissipating and cooling performance. In addition, the inter-fin space is extremely narrow to minimize size
25 of the heat exchanger. Therefore, when an evaporator is operated, moisture in the atmosphere condenses in the fin gaps. The condensed water tends to form water drops which make clogging of the fin gaps more liable to occur, as the hydrophobic property of the fin surface is higher. As a result, the ventilation resistance of the fin gaps is increased, which reduces the heat-exchanging
30 efficiency. A further problem is incurred such that the water drops are scattered downstream of the air flow.

- Several methods are therefore proposed and implemented for imparting hydrophilic property on the surface of the metallic material and hence improving its water wettability. These methods aim to prevent the water drops from being
35 retained in the fin gaps and hence to prevent the occurrence of clogging.

The methods for imparting hydrophilic property to the metallic material are classified into two. One is adding or incorporating an organic polymer to an inorganic compound, particularly alkali silicate. The other method relies solely on the organic compound. The former method, which relies on adding or incorporating an organic polymer to alkali silicate, provides improved hydrophilic property and durability of the hydrophilic property, but involves a problem of foreign odor, which is presumed to arise from the inorganic compound, and a problem of lubrication. The latter method, which relies on solely on the organic polymer, exhibits improved hydrophilic property and no problems regarding foreign odor, and lubrication, but the corrosion resistance of a film consisting solely of an organic compound is poor. A dual coating method is, therefore, employed usually such that chemical conversion treatment employed as a pretreatment imparts the corrosion resistance. However, the dual coating method is disadvantageously expensive and moreover of low productivity. In addition, since the chromic-acid chromate and phosphoric-acid chromate, which are usually used in the chemical conversion treatment, contains hexavalent chromium harmful to the human body, there is a possibility that the environment, waste-liquid treatment and the like are detrimentally influenced.

Various methods have been proposed to solve these problems. For example "A Treatment Method by an Aqueous Hydrophilization Treating Agent Having Corrosion Resistance" is disclosed in Japanese Unexamined Patent Publication No. 63-171684. This method resides in that a film on the aluminum or its alloy formed by means of resin synthesized from particular monomers impart corrosion resistance and hydrophilic property to the aluminum and the like. However, the hydrophilic property provided by this method is not yet satisfactory. Generally speaking, the film is used in many cases as the underlying layer of the hydrophilic film.

In addition, Japanese Unexamined Patent Publication No. 6-116527 entitled "Surface Treatment Method for Imparting Hydrophilic Property to the Surface of Aluminum Material" discloses to form a film, which imparts the corrosion resistance and hydrophilic property, by an acrylic-acid monomer, alkali silicate and a cross-linking agent consisting of a vanadium compound. However, the foreign odor and lubrication of this method is unsatisfactory, because they are detrimentally influenced by the inorganic component contained.

In addition, Japanese Unexamined Patent Publication No.1-270,977

entitled "A Hydrophilization Method of Aluminum or its Alloy Having Improved Both Hydrophilic Property and Corrosion Resistance" discloses to form a film, which can impart corrosion resistance and hydrophilic property, by a particular polymer P1, a polymer P2 having a particular functional group and a cross-linking agent. However, since hexavalent chromium is contained in the hydrophilic film, the method is not environmentally-friendly.

As is described above, there is not yet developed, in the heat exchanger made of metallic material, that is, aluminum, the composition of a hydrophilization agent, free of chromium, which can impart improved corrosion resistance and also can maintain the hydrophilic property for an extended period of time.

Summary of the Invention

The present invention intends to solve the problems involved in the prior art described hereinabove. More specifically, it is an object of the present invention to solve such problems as reduction in the heat-exchanging efficiency due to the condensed water, scattering water drops, and generation of foreign odor, and problems in the production process, and the like, and to provide a hydrophilization agent, a hydrophilization liquid free of chromium, which can impart improved hydrophilic property and corrosion resistance, and such hydrophilization method, a metallic material and a heat exchanger,

The present inventors gave extensive considerations to a solution of the above-described problems and discovered that these problems can be solved by means of applying on the surface of metallic material a hydrophilization agent which contains a hydrophilic polymer having a particular non-ionic functional group, a water-soluble polymer having a particular ionic functional group, a vanadium compound, and a compound having at least one element selected from Zr, Ti, Si. Thus, the present invention was completed.

Namely, the hydrophilization agent of metallic material according to the present first invention characterized in that it contains:

(A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;

(B) a hydrophilic polymer having at least one ionic functional group selected

from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;

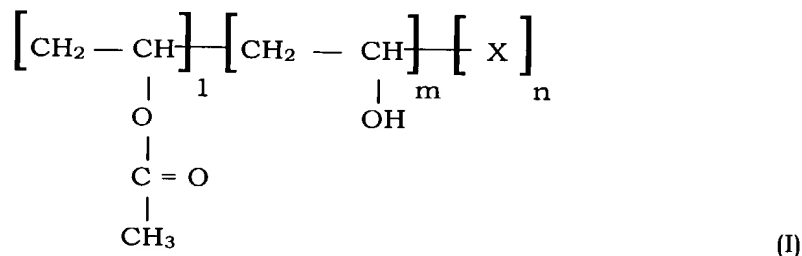
(C) a vanadium compound; and,

(D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

The present invention is described hereinafter in detail.

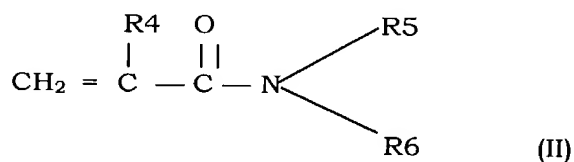
Detailed Description of the Invention

Preferably, the hydrophilic polymer having said a non-ionic functional group (A) in said hydrophilization agent is at least one selected from the polyvinyl alcohol polymer expressed by the following general formula (I) and a reaction product of the polyvinyl alcohol polymer expressed by the following general formula (I) and a diketene.



In the above formula (I), X indicates a copolymerizing unit other than vinyl acetate and vinyl alcohol, and l, m and n indicate the copolymerizing number of the moles of a vinyl acetate copolymerizing unit, a vinyl alcohol polymerizing unit, and the copolymerizing unit X, respectively, $l+m+n = 100$, and l and n may be zero.

Preferably, the hydrophilic polymer having a non-ionic functional group (A) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following general formula (II).



R4 indicates a hydrogen atom or CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 – C4, a benzil group, or a hydroxyalkyl group of C1 – C3.

At least one additive selected from the group consisting of (E) an anti-bacteria/mildew agent, an organic crosslinking agent and a surfactant is preferably contained in addition to the above-mentioned compositions (A) – (D).

Preferably, in the treatment agent according to the present invention, relative to 100 parts by weight of the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements are blended in the weight proportions.

A hydrophilization liquid according to the present second invention is related to the above-described treatment agent which is applied to form a hydrophilic film on the surface of metallic material and is characterized in that it contains from 0.05 to 50g/L of the hydrophilic copolymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the hydrophilic polymer having an ionic functional group (B) as a solid matter, from 0.05 to 10 g/L of the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of a compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements.

A hydrophilization method of metallic material according to the present third invention is characterized in that the hydrophilization agent of metallic material set forth in any one of claims 1 through 5 is deposited on the surface of the metallic material and is dried to form a hydrophilic film having improved corrosion resistance.

The present fourth invention relates to a metallic material, on which surface a hydrophilic film is formed by means of depositing the hydrophilization agent on the surface of the metallic material and drying the same. The present fifth invention relates to a heat exchanger with a hydrophilic film formed as well.

The contents of the present invention are described in detail hereinunder in detail. First, the hydrophilization agent of the first invention is described.

Preferably, the hydrophilic polymer having the non-ionic functional group

and used in the present invention as the first component contains at least one of:
(A-1) which is the polyvinyl alcohol polymer expressed by the above-mentioned
general formula (I), and a reaction product of the polyvinyl alcohol polymer and
diketene; (A-2) which is a co-condensed polymer of at least one acrylamide
polymer selected from a water-soluble polymer and a water-soluble copolymer of
an acrylamide compound expressed by the following above-mentioned general
formula (II), and polyethylene oxide, polyethylene glycoldiamine, adipic acid and
 ϵ -caplactum.

A partially saponified product and completely saponified product of polyvinyl
acetate in the first component (A-1), as well as a partially saponified product and
completely saponified product of a copolymer of vinyl acetate and another
monomer are included in the first component (A-1). A comonomer, which is
copolymerized with the vinyl acetate, is not particularly limited but the following
can be listed: acrylic acid, methacrylic acid, itaconic acid, maleic acid, or their
salts as the anionic comonomer; styrene, acrylonitrile, vinyl ether,
(meth)acrylamide, N-methylol (meth)acrylamide, methyl (meth)acrylate,
hydroxyethyl (meth)acrylate, vinyl pyrrolidone, acryloyl morpholine, and vinyl
acetate as the non-ionic monomer; and aminoethyl (meth)acrylate, vinylimidazole,
and N, N-dimethyl diallylamine as the cationic comonomer.

In the above formula (I), X indicates a polymerizing unit other than vinyl
acetate and vinyl alcohol; l, m and n indicate the co-polymerizing number of the
moles of a vinyl-acetate polymerizing unit, a vinyl-alcohol unit, and the co-
polymerizing unit, respectively. The copolymerizing mole ratio ($n/(l+m+n)$) of the
copolymerizing unit (X) is preferably from 0 to 0.4 and is more preferably from 0 to
0.3. In addition, the copolymerizing mole ratio ($l/(l+m+n)$) of the vinyl acetate
polymerizing unit is preferably from 0 to 0.2 and is more preferably from 0 to 0.1
in the polyvinyl alcohol polymer of the general formula (I). When these co
polymerizing ratios are excessively large, the water solubility of the resultant
polyvinyl alcohol compound may be lowered to an unsatisfactory level. The range
of the mole ratio ($m/(l+m+n)$) of the vinyl alcohol polymerizing unit is determined
by the above-mentioned two mole ratios.

Next, the first component (A-2) is at least one acrylamide polymer selected
from a water-soluble polymer and a water-soluble copolymer of an acrylamide
compound expressed by the general formula (II) mentioned above.

Here, in the above-mentioned general formula (II), R4 indicates a hydrogen

atom or a CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 – C4, a benzil group, or a hydroxyalkyl group of C1 – C3. One polymerized product of acrylamide compound (monomer (a-a)) and a copolymerized product of two or more of acrylamide compounds (monomer (a-a)), as well as a copolymer of one or more of an acrylamide compound (monomer (a-a)) according to the general formula (II) and one or more other comonomer (a-b) are included in the general formula (II). The comonomer (a-b) used here is selected from anionic, non-ionic and cationic addition-polymerizing monomers which are polymerizable with the acrylamide monomers (a-a). Such comonomer (a-b) can be selected, for example, from anionic unsaturated monomers such as (meth)acrylic acid, itaconic acid, maleic acid, vinyl sulfonic acid, styrene sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonate acrylamide, 2-acrylamide-2-methylpropane-sulfonate, acid-phosphooxyethyl methacrylate, or their salt, non-ionic unsaturated monomers such as (meth)acryl amide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylate, vinyl pyrrolidone, acryloyl morpholine, polyoxyethylene glycolacrylate, and polyoxyethylene glycolacrylate alkylphenylether, and cationic unsaturated monomers such as aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl-aminoethyl(meth)acrylate, N-hydroxymethyl-aminoethyl methacrylate, vinyl imidazole, vinyl pyridine, N, N-diallyl amine, and N, N-diallyl-N, N-dimethyl ammonium chloride. In addition, the comonomer (a-b) may be selected from such addition-polymerizable monomers not having high hydrophilic property as styrene, acrylonitrile, vinylether, acrylester group and vinylacetate. In this case, the copolymerizing ratio of the comonomer used is selected to maintain the water solubility of the resultant copolymer to the desired level.

One polymer and two or more copolymers of the above-mentioned acrylamide monomer (a-a) mentioned above, as well as a copolymer of one of more of the acrylamide monomer (a-a) and the comonomer (a-b) may be subjected to a post-treatment or post-reaction to change their structure. The so-treated copolymer may be used as the hydrophilic polymer having a non-ionic functional group (A), for example as follows: a reaction product, which is obtained by bringing an amine group and formalin into reaction with the amide group, and which is converted to an aminoalkyl group (Mannich reaction); the amide group, which is converted to an amino group by a decarboxylation reaction, causing alkyl

and bromine to react with the amide group (Hofmann reaction); the side-chain ester group, which is converted to an amino group by an ester-amide interchange reaction, causing the alkyldiamine to react with the side-chain ester group; and a quaterized amino group.

5 The hydrophilic polymer having an ionic functional group (B) and constituting the second component used in the inventive hydrophilization agent has at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group.

10 The hydrophilic polymer having an ionic functional group (B) of the second group is largely classified into (B-1), a polymer not having a cationic group but having at least one ionic functional group selected from the anionic group which consists of a sulfonic acid group, a phosphonic acid group and a carboxyl group, and (B-2), a polymer not having an anionic group and having at least one member selected from the group of a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group. In the second component used in the present invention, it is desirable that the above-mentioned anionic hydrophilic polymer (B-1) and the above-mentioned cationic hydrophilic polymer (B-2) are not used in combination.

20 The anionic monomer (b-1), which forms the anionic hydrophilic polymer not having a cationic group (B-1), can be selected from vinyl sulfonate, styrene sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonic acrylamide, 2-acrylamide-2-methyl propane sulfonate, vinylphenol sulfonate, acid phosphoxy ethylmethacrylate and their salts.

25 The cationic monomer (b-2), which forms the cationic hydrophilic polymer (B-2) can be selected from aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl aminoethyl(meth)acrylate, N-hydroxymethyl aminoethyl methacrylate, vinylimidazole, vinylpyridine, N, N diallylamine, and N, N-diallyl-N, N-dimethylammonium chloride. Each of these monomers (b-1) and (b-2) may form a hydrophilic homopolymer and may be copolymerized with a polymerizable comonomer to form a hydrophilic polymer. The above-mentioned comonomer includes the above-mentioned monomer (b-1) and (b-2) as well as other monomers (b-3), for example, acrylamide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylate, vinylpyrrolidone, acryloyl morpholine, polyethylene glycol acrylate

alkylphenyether, acrylic acid, methacrylic acid, itaconic acid, maleic acid, their salts, styrene, acrylonitrile, vinyl ether, acryl ester group, vinyl acetate and the like. The comonomer may be a low-hydrophilic monomer such as styrene, acrylonitrile, vinyl ether and (meth)acryl esters. When such low hydrophilic monomer is used, its co- polymerizing ratio is set so as not to impair the desired water solubility of the resultant copolymer.

The vanadium compound C which is the third component used in the hydrophilization agent of the present invention, is an inorganic or organic compound which contains vanadium having a possible valence. Metavanadic acid, vanadic acid and its salt (sodium, potassium, ammonium), vanadium oxide such as vanadium pentaoxide, halides such as vanadium pentachloride and vanadium pentafluoride, organic vanadium compounds such as vanadic acetylacetate and vanadyl acetyl acetate, vanadyl sulfate, vanadium sulfate, vanadium nitrate, vanadium phosphate, vanadium acetate, and vanadium biphosphate can be listed.

A reducing agent may be used in combination with the above-mentioned vanadium compound to partially or completely reduce the vanadium compound, as a means for incorporating it into the hydrophilization agent according to the present invention. The reduced vanadium compound is thus included in the hydrophilization agent.

The fourth component contained in the hydrophilization agent of the present invention is a compound having at least one element selected from the group consisting of Zr, Ti, Si. This is a water-soluble or water-dispersing compound. Preferably, for example, zirconium compounds such as zirconium- ammonium carbonate, zirconyl nitrate, zirconyl sulfate, zirconyl nitrate, zirconium fluoric acid, and their salts, a titanium compound such as diisopropoxy titanium- bis acetylacetone, fluoro titanic acid and their salts, silicofluoric acid and its salt, and alkali silicate are used as the compound.

An anti-bacteria agent and/or anti-mildew agent as the fifth component may be added into the hydrophilization agent according to the present invention so as to suppress the putrefaction odor due to propagation of mildew, bacteria and yeast, provided that the effects of the present invention are not impeded by the fifth component. Desirably, the anti-bacteria/mildew agent usable in the present invention is such that it can resist, during the drying step after applying the inventive treatment agent, the heating for removing the water, which is a solvent

of the treatment agent. That is, the anti-bacteria/mildew agent desirably does not have a decomposition temperature at 100 °C or less.

An anti-bacteria and/or mildew agent, which is added in the hydrophilization agent according to the present invention, can be selected, for example, from 5-chloro-2methyl-4-isothiazoline-3-on, 2-methyl-4-isothiazoline-3-on, 2-(4-thiocyano-methylthio)benzothizole, 2, 2-dibromo-3-nitrilopropion amide, sodium ethylene bis(dithiocarbamate), sodium-2-pyridinethiol-1-oxide, zinc-2-pyridinethiol-1-oxide, 2, 2'- dithiobis (pyridine-1-oxide), 2, 4, 5, 6-tetrachloro isophthalonitrile, 2-methylcarbonyl aminobenzimidazole, 2, 3, 5, 6-tetrachloro-4-(methylsulfonyl)-pyridine, 2-(4-thiazolyl) benzimidazole, N-(fluoro dichloromethyl thio) sulfamide, p-chloro-m-xyleneol, dehydroacetic acid, o-phenyl phenol, 1, 2-benzisothiazoline barium, diiodemethyl-p-toulenesulfone, 2-n-octyl-4-isothiazoline-3-on, and 10, 10' oxybisphenoxyarsine and the like.

The addition amount of the anti-bacteria and mildew agent is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore, preferably from 0.5 to 30% by weight based on the total of the first component (A) and the second component (B).

In the present invention, a three-dimensional structure can be formed by utilizing a functional group of the A component, thereby enhancing the water resistance of the film. A water-soluble cross-linking agent can be used for such purpose.

The cross-linking agent, which is included in the hydrophilization agent according to the present invention, can be selected from water-soluble blocked polyisocyanate, polymethylol, polyglycidyne, polyaziridile compound, and an aldehyde group. That is, an organic cross-linking agent can be selected from block polyisocyanate bisulfate, methylol melamine, methylol urea, methylolized polyacrylamide, polyethylene glycol glycidyl ether, diaziridilated polyethylene oxide, glyoxal, furfural and the like.

The addition amount of the cross-linking agent is preferably from 0.1 to 70% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B). When the addition amount is less than 0.1% by weight, the cross-linking effect is insufficient. When the addition amount exceeds 70% by weight, the film becomes too hard and brittle and is not preferable in terms of formability and adhesiveness.

If necessary to further improve the lubrication property of the film formed by

using the hydrophilization agent according to the present invention, or to improve the coating performance of the agent, a surfactant may be added. The surfactant used for this purpose may be any one of the anionic, cationic, non-ionic or amphoteric surfactant. However, it is not preferable to use a surfactant having an ionic property opposite to that of the polymer of the components (A) and (B) used in combination with the surfactant, since the stability of the treating liquid may be impeded.

The following are examples of surfactant capable of adding into the hydrophilization agent according to the present invention: non-ionic surfactant such as polyoxy-ethylene alkylether, e.g., polyoxyethylene laurylether and polyoxyethylene stearylether, polyoxyethylene alkylphenylether, e.g., polyoxyethylene nonylphenylether, sorbitan fatty ester, e.g., a block polymer of oxyethylene and oxypropylene (PLURONIC), sorbitan monolaurate and sorbitan monostearate, fatty ester of polyoxyethylene, e.g., polyoxyethylene laurate, polyoxyethylene stearate, and polyoxyethylene oleate, glycerin fatty ester, and polyoxethylene propylene glycol alkyl phenol ether; anionic surfactant such as fatty salt, e.g., sodium laurate, sodium stearate and sodium oleate, alkyl sulfate, e.g., sodium dodecylsulfate, alkylsulfosuccinate, dialkylsulfosuccinate, alkenylsulfosuccinate and polyoxyethylene alkyl sulfate; cationic surfactant such as alkylamine salt, e.g., stearylamine acetate, quaternary ammonium salt, e.g., stearyltrimethyl ammonium, alkylbetaine, e.g., lauryl betaine, and amine oxide; and, amphoteric surfactant such as aminopropionate and alkyl dimethyl betaine. In addition, the fluorine-based surfactant and the silicon-based surfactant can be used. The addition amount of the surfactant used is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore preferably from 0.5 to 30% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B).

In the hydrophilization agent according to the present invention, it is preferred that, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the second component, i.e., the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the

elements, are blended in the weight proportions. More preferably, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), the second component, i.e., the hydrophilic polymer having an ionic functional group (B) is from 1 to 100 parts by weight, the third component, i.e., the vanadium compound (C) is from 1 to 100 parts by weight in terms of vanadium ions, and the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si is from 1 to 100 parts by weight in terms of the elements.

The hydrophilization liquid according to the present invention preferably contains from 0.05 to 50g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.05 to 10 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements. More preferable ranges of the concentrations are: from 0.5 to 10g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.5 to 10g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.5 to 5 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.5 to 5 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements.

The solvent of the hydrophilization agent according to the present invention is mainly composed of water. The combination of water and a water-soluble solvent such as alcohol, ketone, CELLOSOLVE and the like in order to adjust the drying speed, to improve the conditions of the coated film, or to enhance the solubility of the components presents no problems. In addition, one or more of a rust preventive, a leveling agent, filler, a coloring agent, an anti-foaming agent and the like may be added into the hydrophilization agent according to the present invention in a range not impairing the gist of the present invention and the film performance.

The hydrophilization agent of the present invention is used as is, or is used as the surface-treatment liquid, in which the agent is diluted with water. The

concentration and the viscosity of the treatment liquid are adjusted appropriately to meet the application method to be employed, the desired film thickness and the like. Preferably, the thickness of the film after drying is from 0.05 to 5 μm , more preferably from 0.1 to 2 μm . When the film thickness is less than 0.05 μm , it is difficult to impart satisfactory hydrophilic property. When the film thickness exceeds 5 μm , there is a possibility that the heat conductivity is inappropriately lowered.

The surface of metallic material to be surface-treated by the present invention is preferably pre-treated by chemical conversion and the like for the purpose of enhancing the corrosion resistance and the like. A chemical conversion treatment agent, which is based on zirconium phosphate, titanium phosphate, vanadium and the like, can be listed as the pre-treatment agent which can enhance the corrosion resistance.

In the hydrophilization method according to the present invention, the surface of the metallic material is degreased, and if necessary, pre-surface treated; subsequently, the hydrophilization agent is deposited on the surface of the metallic material and is then heated and dried to form a film.

The application method of the aqueous treatment agent is not particularly limited, and such methods as dipping, spraying, brushing, roll-coating, flow-coating and the like can be used.

The drying method after application of the hydrophilic treatment agent is not particularly limited. Usually, a hot-blast drying oven and the like are used to dry at a temperature of from 80 to 300°C, more preferably from 100 to 250°C to form a film.

Best Mode for Carrying Out Invention

The present invention is further explained with reference to the following examples, which however do not limit the present invention.

Examples 1 – 9 and Comparative Examples 1 - 5

In each of Examples 1 – 9 and Comparative Examples 1 – 5, the metallic material was subjected to the following pre-treatment. After the pre-treatment, the following hydrophilization agents were used to prepare the surface-treated metallic materials. The tests described below were carried out.

(1) Pre-treatments

The pre-treatment by the methods shown in Table 1 and Table 2 was

applied to various metallic materials.

Pre-treatment (A)

Al-Mn based alloy sheets (JIS-A3004, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned Al-Mn based alloy sheets were dipped for 60 seconds in the aqueous solution, which was held at 40°C and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name – N405, a product of Nihon Parkerizing Co., Ltd.), followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate film (from 30 to 40 mg/m² in terms of the depositing amount of zirconium) was formed on the surface of the aluminum sheets.

Pre-treatment (B)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned aluminum sheets were dipped for 60 seconds in the aqueous solution, which was held at 50°C and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name – N405, a product of Nihon Parkerizing Co., Ltd.), followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate film (from 25 to 35 mg/m² in terms of the depositing amount of zirconium) was formed on the surface of the aluminum sheets.

Pre-treatment (C)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. Drying was carried out at 80°C for 30 seconds.

(2) Hydrophilization Treatment

The hydrophilization treatment by the following methods was applied to the metallic material, which had been pre-conditioned as described above. The treatment methods used are shown in Fig. 1 (Table 1) and Fig. 2 (Table 2).

Hydrophilization Method (A)

The hydrophilization liquid was adjusted to have 3% of total nonvolatile matter content. Immersion in the hydrophilization liquid was carried out at room temperature for 10 seconds. Setting was carried out for approximately 20 seconds, and the heating and drying were then carried out at 160°C for 5 minutes. Incidentally, the target amount of the hydrophilic film was from 0.3 to 0.5 g/m².

Hydrophilization Method (B)

The hydrophilization liquid was adjusted to have 7% of total nonvolatile matter content. Bar-coating was carried out using a bar-coater No. 3 (the target value of wet application amount was 4.5mL/m²). The heating and drying were then carried out at 200°C for 10 seconds.

(3) Components of Hydrophilization Agent

The treatment agents were adjusted using the following components and additives. The composition of the treatment liquid is shown in Table 1 and Table 2.

(A) Components of Hydrophilic Polymer having a Non-ionic Functional Group

- 1 Polyvinyl alcohol (saponification degree – 90 mol %, molecular-weight – 100,000)
- 2 5 mol % - diketene-treated polyvinyl alcohol (saponification degree – 90 mol %, molecular-weight – 50,000)
- 3 acrylamide polymer (molecular weight – 70,000)
- 4 acrylamide/acrylic acid = 50/50 (molecular weight = 50,000)

(B) Components of Hydrophilic Polymer having an Ionic Functional Group

Polymer having an Anionic Hydrophilic Functional Group (B-1)

- 1 Copolymer of acrylic acid/sulfoethyl methacrylate (80/20) (Molecular weight – 70,000)
- 2 Copolymer of acrylic acid/sodium vinylsulfonate (60/40) (Molecular weight – 30,000)
- 3 Sodium polystyrene sulfonate (molecular weight – 50,000)

Polymer having a Cationic Hydrophilic Functional Group (B-2)

4 Polydimethyl diallyl ammonium chloride (molecular weight – 20,000)

5 Block polymer of adipic acid, amino ethyl piperazine and ϵ -caprolactum (molecular weight – 10,000)

5 (C) Vanadium Compound

1 Sodium vanadate

2 Ammonium metavanadate

(D) Compound having at least one element selected from the group consisting of Zr, Ti, Si

10 1 Titanium fluoroammonium

2 Fluoro zirconate

3 Ammonium zirconium carbonate

(E) Additive

Anti bacteria Agent

15 1 Zinc-2-pyridinethiol-1-oxide

2 2-n-octyl-4-isothizaoline-3-on

3 2,2-dibromo-3-nitrylopropylamide

(Organic cross-linking agent)

4 Glyoxal

20 5 Polyethylene glycol-polyisocyanate prepolymer, block polymerized by sodium sulfite (isocyanate content: 5.0 –5.5)

(Surfactant)

6 DISCOL R-612, product of Daiichi Industry Pharmacy Co., Ltd. (non-ionic surfactant)

25 (4) Test and Evaluation

The following tests and evaluation were carried out for the treatment sheets, which were prepared in each of Examples 1 – 9 and Comparative Examples 1 – 5. The test results are shown in Table 3 and Table 4.

(Hydrophilic Property)

30 The treated materials for the test were immersed in flowing water at room temperature for 8 hours, followed by drying at 80°C for 16 hours, as one cycle of the treatment. Five cycles of treatment were carried out. The contact angle of water on the surface of the resultant test samples was measured by using an image-processing type contact-angle meter CA-X (Product of Kyowa Interface
35 Chemistry Co., Ltd.)

(Prevention of Foreign Odor Generation)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80°C for 1 hour and exposure to the water vapor of boiled de-ionized water for 1 second. The foreign odor was quickly smelled and evaluated.

Evaluation Criterion

◎ No appreciable foreign odor

△: Somewhat appreciable foreign odor

×: Evidently appreciable foreign odor

(Corrosion Resistance)

The salt-spray test based on JIS-Z-2371 was carried out. After spraying for 240 hours, the state of white rust generation on the samples was evaluated.

Evaluation Criterion

: No generation of white rust

o: Less than 10% of generated area of white-rust

△: From 10 to less than 30% of generated area of white rust

×: 30% or more of generated area of white rust

(Anti-bacteria Property)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80 °C for 1 hour. The so-treated materials were cut into 3 cm squares. Nutrient Broth and a 1: 1 mixture liquid of heptone and glucose were used as the nutrient source of bacteria and mildew, respectively. The nutrient source was deposited on the surface of the test pieces, and a mixed suspension liquid of the following bacteria was sprayed on the deposited nutrient source. Culture was carried out at 30°C ± 2°C for 14 days. The bacteria was extracted from the post-cultured treated sheets into the bacteria-controlled water. The number of bacteria in the bacteria-controlled water was measured by using a dilution culture method.

Evaluation Criterion

o: Less than $10^2/\text{m}^2$ of the bacteria number

△: Not less than $10^2/\text{m}^2$ and less than $10^5/\text{m}^2$ of the bacteria number

×: Not less than $10^5/\text{m}^2$ of the bacteria number

Bacteria Used

Bacteria: Escherishia coli, Bacillus subtilis

Pseudomonas aeruginosa

Mildew: *Aspergillus niger*, *Penicillium citrinum*

Cladosporium cladosporioides

As is apparent from the results of Table 3 and Table 4, the treated materials obtained in Examples 1 – 9, in which the inventive hydrophilization agent and treatment method were used, exhibit improved hydrophilic property even under the durability test conditions and improved property for prevention of foreign odor. The corrosion resistance test also revealed improved resistance. Contrary to these results, the durability of the film was poor, and the preventive property of foreign odor and the corrosion resistance failed in Comparative Examples 1, and 4, in which no hydrophilic polymer component having a non-ionic functional group (A) was used. The hydrophilic property of the resultant film was unsatisfactory in Comparative Example 2, in which no polymer component having an ionic functional group (B) was used. The corrosion resistance of the resultant film was poor in Comparative Example 3, in which no vanadium-compound component was used, and in Comparative Example 5, in which no compound containing at least one element selected from the group consisting of Zr, Ti, Si (D) was used.

Industrial Applicability

The hydrophilization agent and the treatment method of the present invention, when applied to the metallic material, particularly the aluminum-containing metallic material, can form on the surface of said metallic material a non-chrome film, which exhibits improved corrosion resistance, hydrophilic property and preventive property of foreign odor for a prolonged period of time, without using a chromic acid film for pre-conditioning.

What is claimed is:

1. A hydrophilization agent for metallic material, comprising:

5 (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of primary amide groups, secondary amide groups, tertiary amide groups, hydroxyl groups and [a] polyoxyalkylene [group] groups;

10 (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of sulfonic acid groups, phosphonic acid groups, carboxyl groups, primary amino groups, secondary amino groups, tertiary amino groups and quaternary ammonium groups;

(C) a vanadium compound; and

15 (D) a compound containing at least one element selected from the group consisting of Zr, Ti, and Si.

20

Abstract of the Disclosure

A hydrophilization agent free of chromium can impart to a heat exchanger made of aluminum, improved corrosion resistance and hydrophilic property lasting for long period of time. The hydrophilization agent contains:

(A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;

(B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;

(C) a vanadium compound; and,

(D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

Table 1 Composition of Hydrophilization Agent of Examples

Exam- ples	Pre- adjust- ing Method	Treat- ment Method	Hydrophilization						
			Composition of Treatment Liquid (weight parts)						Active Agent
			(A)	(B)	(C)	(D)	(E)		
							Anti- mildew Agent	Cross- linking Agent	
1	A	A	① (50)	① (25)	① (4)	① (8)	① (3)	④ (10)	
2	B	A	① (25)	② (40)	① (25)	③ (10)	③ (3)	⑤ (5)	⑥ (2)
3	C	A	② (40)	① (20)	② (15)	② (15)	② (5)	⑤ (5)	
4	B	B	② (40)	③ (30)	① (12)	② (8)		④ (6)	
5	B	A	③ (35)	④ (35)	② (10)	② (10)	② (3)	④ (5)	⑥ (2)
6	A	A	② (50)	⑤ (20)	② (10)	① (5)	① (5)	④ (10)	
7	C	A	④ (20)	① (25)	② (25)	① (18)	③ (4)	④ (8)	
8	B	A	④ (30)	③ (35)	① (15)	② (8)	① (3)		
9	A	A	① (20)	② (20)	② (10)	④ (5)	③ (3)		⑥ (2)

Table 2 Composition of Hydrophilization Agent of Comparative Examples

Comparative Examples	Pre-adjusting Method	Treatment Method	Hydrophilization					
			Composition of Treatment Liquid (weight parts)					
			(A)	(B)	(C)	(D)	(E)	
1	A	A	—	① (25)	① (4)	① (8)	① (3)	④ (10)
2	B	A	① (25)	② —	① (25)	③ (10)	③ (3)	⑤ (5) ⑥ (2)
3	B	A	③ (35)	④ (35)	② —	② (10)	② (3)	④ (5) ⑥ (2)
4	A	A	③ —	⑤ (20)	② (10)	① (5)	① (5)	④ (10)
5	B	A	④ (30)	③ (35)	① (15)	② —	① (3)	④ (9)

Table 3 Test Result of Examples

Examples	Test Result				
	Hydrophilic Property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	20-24	○	◎	○
2	<5	12-18	○	◎	○
3	<5	19-25	○	○	○
4	<5	16-21	○	◎	×
5	<5	14-18	○	◎	○
6	<5	22-25	○	◎	○
7	<5	20-25	○	○	○
8	<5	23-26	○	◎	○
9	<5	18-20	○	○	○

Table 4 Test Result of Comparative Examples

Comparative Examples	Test Result				
	Hydrophilic property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	30-38	×	△	×
2	20-25	35-48	○	◎	○
3	<5	14-20	○	×	○
4	<5	32-39	×	△	×
5	<5	21-25	○	×	○

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Hydrophilization Agent [of] for Metallic Material[, Hydrophilization Liquid,
Hydrophilization Method, Metallic Material and Heat Exchanger]

This application claims priority from Japanese applications 10/293656, filed 15
October 1998, and 11/288204, filed 8 October 1999, and International
application PCT/JP00/05652, filed 8 October 1999.

[Technical] Field of the Invention

The present invention relates to a hydrophilization agent, a hydrophilization
liquid and a hydrophilization method of metallic material, a metallic material and
a heat exchanger. More particularly, the present invention relates to a
hydrophilization agent, a hydrophilization liquid free of chromium, which can
impart improved hydrophilic property and corrosion resistance to the metallic
material, for example the aluminum-based metallic material used for the fins of a
heat exchanger. The present invention relates to such metallic material and heat
exchanger.

[Background Technique] Discussion of the Related Art

Heretofore, heat exchangers are manufactured by bonding, e, g., brazing,
the metallic material, e.g., an aluminum-based metallic material. Most of such
heat exchangers are so designed that their heat dissipating and cooling portions
have surface area as large as possible to enhance the heat dissipating and cooling
performance. In addition, the inter-fin space is extremely narrow to minimize size
of the heat exchanger. Therefore, when an evaporator is operated, moisture in the
atmosphere condenses in the fin gaps. The condensed water tends to form water
drops which make clogging of the fin gaps more liable to occur, as the
hydrophobic property of the fin surface is higher. As a result, the ventilation
resistance of the fin gaps is increased, which reduces the heat-exchanging
efficiency. A further problem is incurred such that the water drops are scattered
downstream [the] of the air flow.

Several methods are therefore proposed and implemented for imparting
hydrophilic property on the surface of the metallic material and hence improving

its water wettability. These methods aim to prevent the water drops from being retained in the fin gaps and hence to prevent the occurrence of clogging.

The methods for imparting hydrophilic property to the metallic material are classified into two. One is adding or incorporating an organic polymer to an inorganic compound, particularly alkali silicate. The other method relies solely on the organic compound. The former method, which relies on adding or incorporating an organic polymer to alkali silicate, provides improved hydrophilic property and durability of the hydrophilic property, but involves a problem of foreign odor, which is presumed to arise from the inorganic compound, and a problem of lubrication. The latter method, which relies on solely on the organic polymer, exhibits improved hydrophilic property and no problems regarding foreign odor, and lubrication, but the corrosion resistance of a film consisting solely of an organic compound is poor. A dual coating method is, therefore, employed usually such that chemical conversion treatment employed as a pretreatment imparts the corrosion resistance. However, the dual coating method is disadvantageously expensive and moreover of low productivity. In addition, since the chromic-acid chromate and phosphoric-acid chromate, which are usually used in the chemical conversion treatment, contains hexavalent chromium harmful to the human body, there is a possibility that the environment, waste-liquid treatment and the like are detrimentally influenced.

Various methods have been proposed to solve these problems. For example "A Treatment Method by an Aqueous Hydrophilization Treating Agent Having Corrosion Resistance" is disclosed in Japanese Unexamined Patent Publication No. 63-171684. This method resides in that a film on the aluminum or its alloy formed by means of resin synthesized from particular monomers impart corrosion resistance and hydrophilic property to the aluminum and the like. However, the hydrophilic property provided by this method is not yet satisfactory. Generally speaking, the film is used in many cases as the underlying layer of the hydrophilic film.

In addition, Japanese Unexamined Patent Publication No. 6-116527 entitled "Surface Treatment Method for Imparting Hydrophilic Property to the Surface of Aluminum Material" discloses to form a film, which imparts the corrosion resistance and hydrophilic property, by an acrylic-acid monomer, alkali silicate and a cross-linking agent consisting of a vanadium compound. However, the foreign odor and lubrication of this method is unsatisfactory, because they are

detrimentally influenced by the inorganic component contained.

In addition, Japanese Unexamined Patent Publication No.1-270,977 entitled "A Hydrophilization Method of Aluminum or its Alloy Having Improved Both Hydrophilic Property and Corrosion Resistance" discloses to form a film, which can impart corrosion resistance and hydrophilic property, by a particular polymer P1, a polymer P2 having a particular functional group and a cross-linking agent. However, since hexavalent chromium is contained in the hydrophilic film, the method is not environmentally-friendly.

As is described above, there is not yet developed, in the heat exchanger made of metallic material, that is, aluminum, the composition of a hydrophilization agent, free of chromium, which can impart improved corrosion resistance and also can maintain the hydrophilic property for an extended period of time.

[Disclosure] Summary of the Invention

The present invention intends to solve the problems involved in the prior art described hereinabove. More specifically, it is an object of the present invention to solve such problems as reduction in the heat-exchanging efficiency due to the condensed water, scattering water drops, and generation of foreign odor, and problems in the production process, and the like, and to provide a hydrophilization agent, a hydrophilization liquid free of chromium, which can impart improved hydrophilic property and corrosion resistance, and such hydrophilization method, a metallic material and a heat exchanger,

The present inventors gave extensive considerations to a solution of the above-described problems and discovered that these problems can be solved by means of applying on the surface of metallic material a hydrophilization agent which contains a hydrophilic polymer having a particular non-ionic functional group, a water-soluble polymer having a particular ionic functional group, a vanadium compound, and a compound having at least one element selected from Zr, Ti, Si. Thus, the present invention was completed.

Namely, the hydrophilization agent of metallic material according to the present first invention characterized in that it contains:

- (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a

polyoxyalkylene group;

(B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;

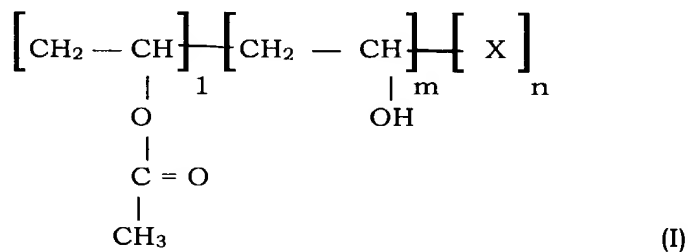
(C) a vanadium compound; and,

(D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

The present invention is described hereinafter in detail.

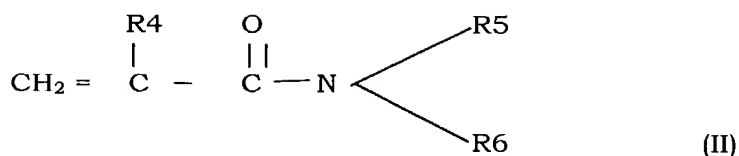
Detailed Description of the Invention

Preferably, the hydrophilic polymer having said a non-ionic functional group (A) in said hydrophilization agent is at least one selected from the polyvinyl alcohol polymer expressed by the following general formula (I) and a reaction product of the polyvinyl alcohol polymer expressed by the following general formula (I) and a diketene.



In the above formula (I), X indicates a copolymerizing unit other than vinyl acetate and vinyl alcohol, and l, m and n indicate the copolymerizing number of the moles of a vinyl acetate copolymerizing unit, a vinyl alcohol polymerizing unit, and the copolymerizing unit X, respectively, $l+m+n = 100$, and l and n may be zero.

Preferably, the hydrophilic polymer having a non-ionic functional group (A) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following general formula (II).



R4 indicates a hydrogen atom or CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 – C4, a benzil group, or a hydroxyalkyl group of C1 – C3.

At least one additive selected from the group consisting of (E) an anti-bacteria/mildew agent, an organic crosslinking agent and a surfactant is preferably contained in addition to the above-mentioned compositions (A) – (D).

Preferably, in the treatment agent according to the present invention, relative to 100 parts by weight of the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements are blended in the weight proportions.

A hydrophilization liquid according to the present second invention is related to the above-described treatment agent which is applied to form a hydrophilic film on the surface of metallic material and is characterized in that it contains from 0.05 to 50g/L of the hydrophilic copolymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the hydrophilic polymer having an ionic functional group (B) as a solid matter, from 0.05 to 10 g/L of the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of a compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements.

A hydrophilization method of metallic material according to the present third invention is characterized in that the hydrophilization agent of metallic material set forth in any one of claims 1 through 5 is deposited on the surface of the metallic material and is dried to form a hydrophilic film having improved corrosion resistance.

The present fourth invention relates to a metallic material, on which surface a hydrophilic film is formed by means of depositing the hydrophilization agent on the surface of the metallic material and drying the same. The present fifth

invention relates to a heat exchanger with a hydrophilic film formed as well.

The contents of the present invention are described in detail hereinunder in detail. First, the hydrophilization agent of the first invention is described.

5 [Embodiments of Invention]

Preferably, the hydrophilic polymer having the non-ionic functional group and used in the present invention as the first component contains at least one of: (A-1) which is the polyvinyl alcohol polymer expressed by the above-mentioned general formula (I), and a reaction product of the polyvinyl alcohol polymer and diketene; (A-2) which is a co-condensed polymer of at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following above-mentioned general formula (II), and polyethylene oxide, polyethylene glycoldiamine, adipic acid and ϵ -caplactum.

15 A partially [sponified] saponified product and completely [sponified] saponified product of polyvinyl acetate in the first component (A-1), as well as a partially [sponified] saponified product and completely [sponified] saponified product of a copolymer of vinyl acetate and another monomer are included in the first component (A-1). A comonomer, which is copolymerized with the vinyl acetate, is not particularly limited but the following can be listed: acrylic acid, methacrylic acid, itaconic acid, maleic acid, or their salts as the anionic comonomer; styrene, acrylonitrile, vinyl ether, (meth)acrylamide, N-methylol (meth)acrylamide, methyl (meth)acrylate, hydroxyethyl (meth)acrylate, vinyl pyrrolidone, [acrloyl] acryloyl morpholine, and vinyl acetate as the non-ionic monomer; and aminoethyl (meth)acrylate, vinylimidazole, and N, N-dimethyl diallylamine as the cationic comonomer.

In the above formula (I), X indicates a polymerizing unit other than vinyl acetate and vinyl alcohol; l, m and n indicate the co-polymerizing number of the moles of a vinyl-acetate polymerizing unit, a vinyl-alcohol unit, and the co-polymerizing unit, respectively. The copolymerizing mole ratio ($n/(l+m+n)$) of the copolymerizing unit (X) is preferably from 0 to 0.4 and is more preferably from 0 to 0.3. In addition, the copolymerizing mole ratio ($l/(l+m+n)$) of the vinyl acetate polymerizing unit is preferably from 0 to 0.2 and is more preferably from 0 to 0.1 in the polyvinyl alcohol polymer of the general formula (I). When these co-polymerizing ratios are excessively large, the water solubility of the resultant

polyvinyl alcohol compound may be lowered to an unsatisfactory level. The range of the mole ratio ($m/(l+m+n)$) of the [vinylalcohol polymerizing unitis] vinyl alcohol polymerizing unit is determined by the above-mentioned two mole ratios.

Next, the first component (A-2) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the general formula (II) mentioned above.

Here, in the above-mentioned general formula (II), R4 indicates a hydrogen atom or a CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 – C4, a benzil group, or a hydroxyalkyl group of C1 – C3. One polymerized product of [acryamide] acrylamide compound (monomer (a-a)) and a [co-poylmerized] copolymerized product of two or more of [acryamide] acrylamide compounds (monomer (a-a)), as well as a copolymer of one or more of an [acryamide] acrylamide compound (monomer (a-a)) according to the general formula (II) and one or more other comonomer (a-b) are included in the general formula (II). The comonomer (a-b) used here is selected from anionic, non-ionic and cationic addition-polymerizing monomers which are polymerizable with the acrylamide momoners (a-a). Such comonomer (a-b) can be selected, for example, from anionic unsaturated monomers such as (meth)acrylic acid, itaconic acid, maleic acid, vinyl sulfonic acid, styrene sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonate acrylamide, 2-acrylamide-2-methylpropane-sulfonate, acid-phosphooxyethyl methacrylate, or their salt, non-ionic unsaturated monomers such as (meth)acryl amide, N-methylol (meth)acrylamide, [hydrdoxyethyl] hydroxyethyl (meth)acrylate, vinyl pyrrolidone, [acrloyl] acryloyl morpholine, polyoxyethylene glycolacrylate, and polyoxyethylene glycolacrylate alkylphenylether, and cationic unsaturated monomers such as aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl-aminoethyl(meth)acrylate, N-hydroxymethyl-aminoethyl methacrylate, vinyl imidazole, vinyl pyridine, N, N diallyl amine, and N, N-diallyl-N, N-dimethyl ammonium chloride. In addition, the comonomer (a-b) may be selected from such addition-polymerizable monomers not having high hydrophilic property as styrene, acrylonitrile, vinylether, acrylester group and vinylacetate. In this case, the copolymerizing ratio of the comonomer used is selected to maintain the water solubility of the resultant copolymer to the desired level.

One polymer and two or more copolymers of the above-mentioned acylamide monomer (a-a) mentioned above, as well as a copolymer of one of more

The hydrophilic polymer having an ionic functional group (B) and constituting the second component used in the inventive hydrophilization agent has at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group.

The hydrophilic polymer having an ionic functional group (B) of the second group is largely classified into (B-1), a polymer not having a cationic group but having at least one ionic functional group selected from the anionic group which consists of a sulfonic acid group, a phosphonic acid group and a carboxyl group, and (B-2), a polymer not having an anionic group and having at least one member selected from the group of a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group. In the second component used in the present invention, it is desirable that the above-mentioned anionic hydrophilic polymer (B-1) and the above-mentioned cationic hydrophilic polymer (B-2) are not used in combination.

The anionic monomer (b-1), which forms the anionic hydrophilic polymer not having a cationic group (B-1), can be selected from vinyl sulfonate, styrene sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonic acrylamide, 2-acrylamide-2-methyl propane sulfonate, vinylphenol sulfonate, acid phosphoxy ethylmethacrylate and their salts.

The cationic monomer (b-2), which forms the cationic hydrophilic polymer (B-2) can be selected from aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl aminoethyl(meth)acrylate, N-hydroxymethyl aminoethyl

methacrylate, vinylimidazole, vinylpyridine, N, N diallylamine, and N, N-diallyl-N, N-dimethylammonium chloride. Each of these monomers (b-1) and (b-2) may form a hydrophilic homopolymer and may be copolymerized with a polymerizable comonomer to form a hydrophilic polymer. The above-mentioned comonomer includes the above-mentioned monomer (b-1) and (b-2) as well as other monomers (b-3), for example, acrylamide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylate, vinylpyrrolidone, [acrloyl] acryloyl morpholine, polyethylene glycol acrylate alkylphenyether, acrylic acid, methacrylic acid, itaconic acid, maleic acid, their salts, styrene, acrylonitrile, vinyl ether, acryl ester group, vinyl acetate and the like. The comonomer may be a low-hydrophilic monomer such as styrene, acrylonitrile, vinyl ether and (meth)acryl esters. When such low hydrophilic monomer is used, its co- polymerizing ratio is set so as not to impair the desired water solubility of the resultant copolymer.

The vanadium compound C which is the third component used in the hydrophilization agent of the present invention, is an inorganic or organic compound which contains vanadium having a possible valence. Metavanadic acid, vanadic acid and its salt (sodium, potassium, ammonium), vanadium oxide such as vanadium pentaoxide, halides such as vanadium pentachloride and vanadium pentafluoride, organic vanadium compounds such as vanadic acetylacetate and vanadyl acetyl acetate, vanadyl sulfate, vanadium sulfate, vanadium nitrate, vanadium phosphate, vanadium acetate, and vanadium biphosphate can be listed.

A reducing agent may be used in combination with the above-mentioned vanadium compound to partially or completely reduce the vanadium compound, as a means for incorporating it into the hydrophilization agent according to the present invention. The reduced vanadium compound is thus included in the hydrophilization agent.

The fourth component contained in the hydrophilization agent of the present invention is a compound having at least one element selected from the group consisting of Zr, Ti, Si. This is a water-soluble or water-dispersing compound. Preferably, for example, zirconium compounds such as zirconium- ammonium carbonate, zirconyl nitrate, zirconyl sulfate, zirconyl nitrate, zirconium fluoric acid, and their salts, a titanium compound such as diisopropoxy titanium- bis acetylacetone, fluoro titanic acid and their salts, silicofluoric acid and its salt, and alkali silicate are used as the compound.

An anti-bacteria agent and/or anti-mildew agent as the fifth component may be added into the hydrophilization agent according to the present invention so as to suppress the putrefaction odor due to propagation of mildew, bacteria and yeast, provided that the effects of the present invention are not impeded by the fifth component. Desirably, the anti-bacteria/mildew agent usable in the present invention is such that it can resist, during the drying step after applying the inventive treatment agent, the heating for removing the water, which is a solvent of the treatment agent. That is, the anti-bacteria/mildew agent desirably does not have a decomposition temperature at 100 °C or less.

An anti-bacteria and/or mildew agent, which is added in the [hydrophillization] hydrophilization agent according to the present invention, can be selected, for example, from 5-chloro-2methyl-4-isothiazoline-3-on, 2-methyl-4-isothiazoline-3-on, [2-(4-thiocyano-mehylthio)benzothizole] 2-(4-thiocyano-methylthio)benzothizole, 2, 2-dibromo-3-nitrilopropyon amide, [sodiumethylene] sodium ethylene bis(dithiocarbamate), sodium-2-pyridinethiol-1-oxide, zinc-2-pyridinethiol-1-oxide, 2, 2'- dithiobis (pyridine-1-oxide), 2, 4, 5, 6-tetrachloro isophthalonitrile, 2-methylcarbonyl aminobenzimidazole, 2, 3, 5, 6-tetrachloro-4-(methylsulfonyl)-pyridine, 2-(4-thyazoly) benzimidazole, N-(fluoro dichloromethyl thio) sulfamide, p-chloro-m-xlenol, dehydroacetic acid, o-phenyl phenol, 1, 2-benzisothiazoline barium, diiodemethyl-p-toulenesulfone, 2-n-octyl-4-isothyazoline-3-on, and 10, 10' oxybisphenoxyarsine and the like.

The addition amount of the anti-bacteria and mildew agent is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore, preferably from 0.5 to 30% by weight based on the total of the first component (A) and the second component (B).

In the present invention, a three-dimensional structure can be formed by utilizing a functional group of the A component, thereby enhancing the water resistance of the film. A water-soluble cross-linking agent can be used for such purpose.

The cross-linking agent, which is included in the hydrophilization agent according to the present invention, can be selected from water-soluble blocked polyisocyanate, polymethylol, polyglycidyne, polyaziridile compound, and an aldehyde group. That is, an organic cross-linking agent can be selected from block [polyisocyante] polyisocyanate bisulfate, methylol melamine, methylol urea, methylolized polyacrylamide, [plyethylene] polyethylene glycol glycidyl ether,

diaziridilated polyethylene oxide, [gloyxal, furfural] glyoxal, furfural and the like.

The addition amount of the cross-linking agent is preferably from 0.1 to 70% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B). When the addition amount is less than 0.1% by weight, the cross-linking effect is insufficient. When the addition amount exceeds 70% by weight, the film becomes too hard and brittle and is not preferable in terms of formability and adhesiveness.

If necessary to further improve the lubrication property of the film formed by using the hydrophilization agent according to the present invention, or to improve the coating performance of the agent, a surfactant may be added. The surfactant used for this purpose may be any one of the anionic, cationic, non-ionic or amphoteric surfactant. However, it is not preferable to use a surfactant having an ionic property opposite to that of the polymer of the components (A) and (B) used in combination with the surfactant, since the stability of the treating liquid may be impeded.

The following are examples of surfactant capable of adding into the hydrophilization agent according to the present invention: non-ionic surfactant such as polyoxy-ethylene alkylether, e.g., polyoxyethylene laurylether and polyoxyethylene [stearyl]ether stearylether, polyoxyethylene alkylphenylether, e.g., polyoxyethylene nonylphenylether, sorbitan fatty ester, e.g., a block polymer of oxyethylene and oxypropylene [(Pluronic)] PLURONIC, sorbitan monolaurate and sorbitan monostearate, fatty ester of polyoxyethylene, e.g., polyoxyethylene laurate, polyoxyethylene stearate, and polyoxyethylene oleate, glycerin fatty ester, and polyoxethylene propylene glycol alkyl phenol ether; anionic surfactant such as fatty salt, e.g., sodium laurate, sodium stearate and sodium oleate, alkyl sulfate, e.g., sodium dodecylsulfate, alkylsulfosuccinate, dialkylsulfosuccinate, alkenylsulfosuccinate and polyoxyethylene alkyl sulfate; cationic surfactant such as alkylamine salt, e.g., stearylamine acetate, quaternary ammonium salt, e.g., stearyltrimethyl ammonium, alkylbetaine, e.g., lauryl betaine, and amine oxide; and, amphoteric surfactant such as aminopropionate and alkyl dimethyl betaine. In addition, the fluorine-based surfactant and the silicon-based surfactant can be used. The addition amount of the surfactant used is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore preferably from 0.5 to 30% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B).

In the hydrophilization agent according to the present invention, it is preferred that, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the second component, i.e., the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements, are blended in the weight proportions. More preferably, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), the second component, i.e., the hydrophilic polymer having an ionic functional group (B) is from 1 to 100 parts by weight, the third component, i.e., the vanadium compound (C) is from 1 to 100 parts by weight in terms of vanadium ions, and the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si is from 1 to 100 parts by weight in terms of the elements.

The hydrophilization liquid according to the present invention preferably contains from 0.05 to 50g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.05 to 10 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements. More preferable ranges of the concentrations are: from 0.5 to 10g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.5 to 10g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.5 to 5 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.5 to 5 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements.

The solvent of the hydrophilization agent according to the present invention is mainly composed of water. The combination of water and a water-soluble solvent such as alcohol, ketone, [cellosolve] CELLOSOLVE and the like in order to

adjust the drying speed, to improve the conditions of the coated film, or to enhance the solubility of the components presents no problems. In addition, one or more of a rust preventive, a leveling agent, filler, a coloring agent, an anti-foaming agent and the like may be added into the hydrophilization agent according to the present invention in a range not impairing the gist of the present invention and the film performance.

The hydrophilization agent of the present invention is used as is, or is used as the surface-treatment liquid, in which the agent is diluted with water. The concentration and the viscosity of the treatment liquid are adjusted appropriately to meet the application method to be employed, the desired film thickness and the like. Preferably, the thickness of the film after drying is from 0.05 to 5 μm , more preferably from 0.1 to 2 μm . When the film thickness is less than 0.05 μm , it is difficult to impart satisfactory hydrophilic property. When the film thickness exceeds 5 μm , there is a possibility that the heat conductivity is inappropriately lowered.

The surface of metallic material to be surface-treated by the present invention is preferably pre-treated by chemical conversion and the like for the purpose of enhancing the corrosion resistance and the like. A chemical conversion treatment agent, which is based on zirconium phosphate, titanium phosphate, vanadium and the like, can be listed as the pre-treatment agent which can enhance the corrosion resistance.

In the hydrophilization method according to the present invention, the surface of the metallic material is degreased, and if necessary, pre-surface treated; subsequently, the hydrophilization agent is deposited on the surface of the metallic material and is then heated and dried to form a film.

The application method of the aqueous treatment agent is not particularly limited, and such methods as dipping, spraying, brushing, roll-coating, flow-coating and the like can be used.

The drying method after application of the hydrophilic treatment agent is not particularly limited. Usually, a hot-blast drying oven and the like are used to dry at a temperature of from 80 to 300°C, more preferably from 100 to 250°C to form a film.

Best Mode for Carrying Out Invention

The present invention is further explained with reference to the following

examples, which however do not limit the present invention.

Examples 1 – 9 and Comparative Examples 1 - 5

In each of Examples 1 – 9 and Comparative Examples 1 – 5, the metallic material was subjected to the following pre-treatment. After the pre-treatment, the following hydrophilization agents were used to prepare the surface-treated metallic materials. The tests described below were carried out.

(1) Pre-treatments

The pre-treatment by the methods shown in Table 1 and Table 2 was applied to various metallic materials.

Pre-treatment (A)

Al-Mn based alloy sheets (JIS-A3004, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – [Fine Cleaner] FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned Al-Mn based alloy sheets were dipped for 60 seconds in the aqueous solution, which was held at 40°C and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name – N405 , a product of Nihon Parkerizing Co., Ltd.) , followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate [film(from) film (from 30 to 40 mg/m² in terms of the depositing amount of zirconium) was formed on the surface of the aluminum sheets.

Pre-treatment (B)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – [Fine Cleaner] FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned aluminum sheets were dipped for 60 seconds in the aqueous solution, which was held at 50°C [an d] and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name – N405, a product of Nihon Parkerizing Co., Ltd.) , followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate film (from 25 to 35 mg/m² in terms of the depositing amount of zirconium) was

formed on the surface of the aluminum sheets.

Pre-treatment (C)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name – [Fine Cleaner] FINE CLEANER 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. Drying was carried out at 80°C for 30 seconds.

(2) Hydrophilization Treatment

The hydrophilization treatment by the following methods was applied to the metallic material, which had been pre-conditioned as described above. The treatment methods used are shown in Fig. 1 (Table 1) and Fig. 2 (Table 2).

Hydrophilization Method (A)

The hydrophilization liquid was adjusted to have 3% of total nonvolatile matter content. Immersion in the hydrophilization liquid was carried out at room temperature for 10 seconds. Setting was carried out for approximately 20 seconds, and the heating and drying were then carried out at 160°C for 5 minutes. Incidentally, the target amount of the hydrophilic film was from 0.3 to 0.5 g/m².

Hydrophilization Method (B)

The hydrophilization liquid was adjusted to have 7% of total nonvolatile matter content. Bar-coating was carried out using a bar-coater No. 3 (the target value of wet application amount was 4.5mL/m²). The heating and drying were then carried out at 200°C for 10 seconds.

(3) Components of Hydrophilization Agent

The treatment agents were adjusted using the following components and additives. The composition of the treatment liquid is shown in Table 1 and Table 2.

(A) Components of Hydrophilic Polymer having a Non-ionic Functional Group

- 1 Polyvinyl alcohol (saponification degree – 90 mol %, molecular-weight – 100,000)
- 2 5 mol % - diketene-treated polyvinyl alcohol (saponification degree – 90 mol %, molecular-weight – 50,000)
- 3 acrylamide polymer (molecular weight – 70,000)

4 acrylamide/acrylic acid = 50/50 (molecular weight = 50,000)

(B) Components of Hydrophilic Polymer having an Ionic Functional Group

Polymer having an Anionic Hydrophilic Functional Group (B-1)

1 Copolymer of acrylic acid/sulfoethyl methacrylate (80/20)
(Molecular weight – 70,000)

2 Copolymer of acrylic acid/sodium vinylsulfonate (60/40)
(Molecular weight – 30,000)

3 Sodium polystyrene sulfonate (molecular weight – 50,000)

Polymer having a Cationic Hydrophilic Functional Group (B-2)

4 Polydimethyl diallyl ammonium chloride (molecular weight –
20,000)

5 Block polymer of adipic acid, amino ethyl piperazine and ϵ -
caprolactum (molecular weight – 10,000)

(C) Vanadium Compound

1 Sodium vanadate

2 Ammonium metavanadate

(D) Compound having at least one element selected from the group
consisting of Zr, Ti, Si

1 Titanium fluoroammonium

2 Fluoro zirconate

3 Ammonium zirconium carbonate

(E) Additive

Anti bacteria Agent

1 Zinc-2-pyridinethiol-1-oxide

2 2-n-octyl-4-isothizaoline-3-on

3 2,2-dibromo-3-nitrylopropylamide

(Organic cross-linking agent)

4 Glyoxal

5 Polyethylene glycol-polyisocyanate prepolymer, block polymerized
by sodium sulfite (isocyanate content: 5.0 –5.5)

(Surfactant)

6 [Discol] DISCOL R-612, product of Daiichi Industry Pharmacy
Co., Ltd. (non-ionic surfactant)

(4) Test and Evaluation

The following tests and evaluation were carried out for the treatment sheets, which were prepared in each of Examples 1 – 9 and Comparative Examples 1 – 5. The test results are shown in Table 3 and Table 4.

(Hydrophilic Property)

The treated materials for the test were immersed in flowing water at room temperature for 8 hours, followed by drying at 80°C for 16 hours, as one cycle of the treatment. Five cycles of treatment were carried out. The contact angle of water on the surface of the resultant test samples was measured by using an image-processing type contact-angle meter CA-X (Product of Kyowa Interface Chemistry Co., Ltd.)

(Prevention of Foreign Odor Generation)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80°C for 1 hour and exposure to the water vapor of boiled de-ionized water for 1 second. The foreign odor was quickly smelled and evaluated.

Evaluation Criterion

○ No appreciable foreign odor

Δ: Somewhat appreciable foreign odor

×: Evidently appreciable foreign odor

(Corrosion Resistance)

The salt-spray test based on JIS-Z-2371 was carried out. After spraying for 240 hours, the state of white rust generation on the samples was evaluated.

Evaluation Criterion

: No generation of white rust

o: Less than 10% of generated area of white-rust

Δ: From 10 to less than 30% of generated area of white rust

×: 30% or more of generated area of white rust

(Anti-bacteria Property)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80 °C for 1 hour. The so-treated materials were cut into 3 cm squares. Nutrient Broth and a 1 : 1 mixture liquid of heptone and glucose were used as the nutrient source of bacteria and mildew, respectively. The nutrient source was deposited on the surface of the test pieces, and a mixed suspension liquid of the following bacteria was sprayed on the deposited nutrient source. Culture was carried out at 30°C ± 2°C for 14 days. The

bacteria was extracted from the post-cultured treated sheets into the bacteria-controlled water. The number of bacteria in the bacteria-controlled water was measured by using a dilution culture method.

Evaluation Criterion

- 5 o: Less than $10^2/\text{m}^2$ of the bacteria number
 Δ: Not less than $10^2/\text{m}^2$ and less than $10^5/\text{m}^2$ of the bacteria
 number
 ×: Not less than $10^5/\text{m}^2$ of the bacteria number

Bacteria Used

- 10 Bacteria: Escherishia coli, Bacillus subtilis
 Pseudomanos aeruginosa
 Mildew: Aspergillus niger, Penicillium critrinum
 Cladosporium cladosporioides

15 As is apparent from the results of Table 3 and Table 4, the treated
materials obtained in Examples 1 – 9, in which the inventive hydrophilization
agent and treatment method were used, exhibit improved hydrophilic property
even under the durability test conditions and improved property for prevention of
foreign odor. The corrosion resistance test also revealed improved resistance.
Contrary to these results, the durability of the film was poor, and the preventive
20 property of foreign odor and the corrosion resistance failed in Comparative
Examples 1, [4] and 4, in which no hydrophilic polymer component having a non-
ionic functional group (A) was used. The hydrophilic property of the resultant film
was unsatisfactory in Comparative Example 2, in which no polymer component
having an ionic functional group (B) was used. The corrosion resistance of the
25 resultant film was poor in Comparative Example 3, in which no vanadium-
compound component was used, and in Comparative Example 5, in which no
compound containing at least one element selected from the group consisting of
Zr, Ti, Si (D) was used.

30 Industrial Applicability

 The hydrophilization agent and the treatment method of the present
invention, when applied to the metallic material, particularly the aluminum-
containing metallic material, can form on the surface of said metallic material a
non-chrome film, which exhibits improved corrosion resistance, hydrophilic
35 property and preventive property of foreign odor for a prolonged period of time,

without using a chromic acid film for pre- conditioning.

[Claims] What is claimed is:

1. A hydrophilization agent [of] for metallic material, [characterized in that it
5 contains] comprising:

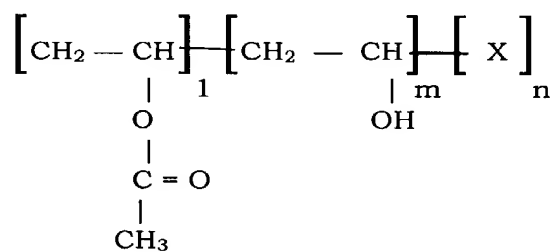
(A) a hydrophilic polymer having at least one non-ionic functional group
selected from the group consisting of [a] primary amide [group] groups,
[a] secondary amide [group] groups, [a] tertiary amide [group] groups, [a]
hydroxyl [group] groups and [a] polyoxyalkylene [group] groups;

10 (B) a hydrophilic polymer having at least one ionic functional group selected
from the group consisting of [a] sulfonic acid [group] groups, [a]
phosphonic acid [group] groups, [a] carboxyl [group] groups, [a] primary
amino [group] groups, [a] secondary amino [group] groups, [a] tertiary
amino [group] groups and [a] quaternary ammonium [group] groups;

15 (C) a vanadium compound; and

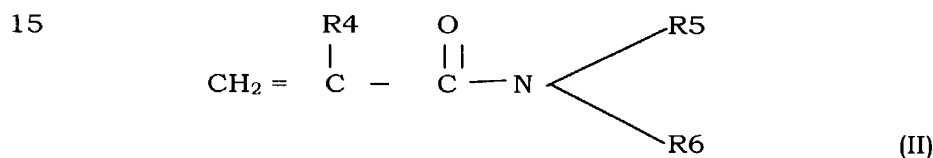
(D) a compound [having] containing at least one element selected from the
group consisting of Zr, Ti, and Si.

[2. A hydrophilization agent according to claim 1, wherein said component
(A) is at least one selected from the polyvinyl alcohol polymer expressed by the
20 following general formula (I) and a reaction product of the polyvinyl alcohol
polymer expressed by the following general formula (I) and a diketene,



5 in the above formula (I), X indicates a copolymerizing unit other than vinyl acetate and vinyl alcohol, and l, m and n indicate the copolymerizing number of the moles of a vinyl acetate copolymerizing unit, a vinyl-alcohol polymerizing unit, and the co polymerizing unit X, respectively, and l and n may be zero.

10 3. A hydrophilization agent according to claim 1, wherein said component (A) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following general formula (II),



25 R4 indicates a hydrogen atom or a CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 - C4, a benzil group, or a hydroxyalkyl group of C1 - C3 .

30 4. A hydrophilization agent according to any one of claims 1 through 3, further containing at least one additive selected from the group consisting of (E) an anti-bacteria/mildew agent, an organic crosslinking agent and a surfactant.

35 5. A hydrophilization agent according to any one of claims 1 through 4, wherein relative to 100 parts by weight of said hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of said hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of said vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of a compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements are blended in the weight proportions.

6. A hydrophilization liquid of metallic material, characterized in that it contains from 0.05 to 50g/L of the hydrophilic copolymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.05 to 10 g/L of the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of the compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements, each set forth in claim 1.

7. A hydrophilization method of metallic material, characterized in that the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 6 is deposited on the surface of the metallic material and is dried to form a hydrophilic film.

8. A metallic material, characterized in that a hydrophilic film is formed on the surface thereof by means of depositing the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 5 on the surface of the metallic material and drying the same.

9. A heat exchanger, characterized in that a hydrophilic film is formed on the surface of a metallic material by means of depositing the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 5 on the surface of the metallic material and drying the same.]

Abstract of the Disclosure

A hydrophilization agent free of chromium can impart to a heat exchanger made of aluminum, improved corrosion resistance and hydrophilic property lasting for long period of time. The [hydrphilization] hydrophilization agent contains:

- (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;
- (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;
- (C) a vanadium compound; and,
- (D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

Table 1 Composition of Hydrophilization Agent of Examples

Exam- ples	Pre- adjust- ing Method	Treat- ment Method	Hydrophilization						
			Composition of Treatment Liquid (weight parts)						
			(A)	(B)	(C)	(D)	(E)		
							Anti- mildew Agent	Cross- linking Agent	Active Agent
1	A	A	① (50)	① (25)	① (4)	① (8)	① (3)	④ (10)	
2	B	A	① (25)	② (40)	① (25)	③ (10)	③ (3)	⑤ (5)	⑥ (2)
3	C	A	② (40)	① (20)	② (15)	② (15)	② (5)	⑤ (5)	
4	B	B	② (40)	③ (30)	① (12)	② (8)		④ (6)	
5	B	A	③ (35)	④ (35)	② (10)	② (10)	② (3)	④ (5)	⑥ (2)
6	A	A	③ (50)	⑤ (20)	② (10)	① (5)	① (5)	④ (10)	
7	C	A	④ (20)	① (25)	② (25)	① (18)	③ (4)	④ (8)	
8	B	A	④ (30)	③ (35)	① (15)	② (8)	① (3)		
9	A	A	① (20)	② (20)	② (10)	④ (5)	③ (3)		⑥ (2)

Table 2 Composition of Hydrophilization Agent of Comparative Examples

Comparative Examples	Pre-adjusting Method	Treatment Method	Hydrophilization					
			Composition of Treatment Liquid (weight parts)					
			(A)	(B)	(C)	(D)	(E)	
1	A	A	—	① (25)	① (4)	① (8)	① (3)	④ (10)
2	B	A	① (25)	② —	① (25)	③ (10)	③ (3)	⑤ (5) ⑥ (2)
3	B	A	③ (35)	④ (35)	② —	② (10)	② (3)	④ (5) ⑥ (2)
4	A	A	③ —	⑤ (20)	② (10)	① (5)	① (5)	④ (10)
5	B	A	④ (30)	③ (35)	① (15)	② —	① (3)	④ (9)

Table 3 Test Result of Examples

Examples	Test Result				
	Hydrophilic Property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	20-24	○	◎	○
2	<5	12-18	○	◎	○
3	<5	19-25	○	○	○
4	<5	16-21	○	◎	×
5	<5	14-18	○	◎	○
6	<5	22-25	○	◎	○
7	<5	20-25	○	○	○
8	<5	23-26	○	◎	○
9	<5	18-20	○	○	○

Table 4 Test Result of Comparative Examples

Comparative Examples	Test Result				
	Hydrophilic property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	30-38	×	△	×
2	20-25	35-48	○	◎	○
3	<5	14-20	○	×	○
4	<5	32-39	×	△	×
5	<5	21-25	○	×	○

Corrected Translation of International Application (Clean Version)

Specification

Hydrophilization Agent of Metallic Material, Hydrophilization Liquid,
Hydrophilization Method, Metallic Material and Heat Exchanger

5

Technical Field

10 The present invention relates to a hydrophilization agent, a hydrophilization liquid and a hydrophilization method of metallic material, a metallic material and a heat exchanger. More particularly, the present invention relates to a hydrophilization agent, a hydrophilization liquid free of chromium, which can impart improved hydrophilic property and corrosion resistance to the metallic material, for example the aluminum-based metallic material used for the fins of a heat exchanger. The present invention relates to such metallic material and heat exchanger.

15

Background Technique

20 Heretofore, heat exchangers are manufactured by bonding, e. g., brazing, the metallic material, e.g., an aluminum-based metallic material. Most of such heat exchangers are so designed that their heat dissipating and cooling portions have surface area as large as possible to enhance the heat dissipating and cooling performance. In addition, the inter-fin space is extremely narrow to minimize size of the heat exchanger. Therefore, when an evaporator is operated, moisture in the atmosphere condenses in the fin gaps. The condensed water tends to form water drops which make clogging of the fin gaps more liable to occur, as the hydrophobic property of the fin surface is higher. As a result, the ventilation resistance of the fin gaps is increased, which reduces the heat-exchanging efficiency. A further problem is incurred such that the water drops are scattered downstream the of air flow .

30 Several methods are therefore proposed and implemented for imparting hydrophilic property on the surface of the metallic material and hence improving its water wettability. These methods aim to prevent the water drops from being retained in the fin gaps and hence to prevent the occurrence of clogging.

35 The methods for imparting hydrophilic property to the metallic material are classified into two. One is adding or incorporating an organic polymer to an inorganic compound, particularly alkali silicate. The other method relies solely on the organic compound. The former method, which relies on adding or incorporating an organic polymer to alkali silicate, provides improved hydrophilic property and durability of the hydrophilic property, but involves a problem of foreign odor, which is presumed to arise from the inorganic compound, and a problem of lubrication. The latter method, which relies on solely on the organic polymer, exhibits improved hydrophilic property and no problems regarding foreign odor, and lubrication, but the corrosion resistance of a film consisting solely of an organic compound is poor. A dual coating method is, therefore, employed usually such that chemical conversion treatment employed as a pretreatment imparts the corrosion resistance. However, the dual coating method is disadvantageously expensive and moreover of low productivity. In addition, since the chromic-acid chromate and phosphoric-acid chromate, which are usually used in the chemical conversion treatment, contains hexavalent chromium harmful to the human body, there is a possibility that the environment, waste-liquid treatment and the like are detrimentally influenced.

50

Various methods have been proposed to solve these problems. For example "A Treatment Method by an Aqueous Hydrophilization Treating Agent Having Corrosion Resistance" is disclosed in Japanese Unexamined Patent Publication

No. 63-171684. This method resides in that a film on the aluminum or its alloy formed by means of resin synthesized from particular monomers impart corrosion resistance and hydrophilic property to the aluminum and the like. However, the hydrophilic property provided by this method is not yet satisfactory. Generally speaking, the film is used in many cases as the underlying layer of the hydrophilic film.

In addition, Japanese Unexamined Patent Publication No. 6-116527 entitled "Surface Treatment Method for Imparting Hydrophilic Property to the Surface of Aluminum Material" discloses to form a film, which imparts the corrosion resistance and hydrophilic property, by an acrylic-acid monomer, alkali silicate and a cross-linking agent consisting of a vanadium compound. However, the foreign odor and lubrication of this method is unsatisfactory, because they are detrimentally influenced by the inorganic component contained.

In addition, Japanese Unexamined Patent Publication No.1-270,977 entitled "A Hydrophilization Method of Aluminum or its Alloy Having Improved Both Hydrophilic Property and Corrosion Resistance" discloses to form a film, which can impart corrosion resistance and hydrophilic property, by a particular polymer P1, a polymer P2 having a particular functional group and a cross-linking agent. However, since hexavalent chromium is contained in the hydrophilic film, the method is not environmentally-friendly.

As is described above, there is not yet developed, in the heat exchanger made of metallic material, that is, aluminum, the composition of a hydrophilization agent, free of chromium, which can impart improved corrosion resistance and also can maintain the hydrophilic property for an extended period of time.

Disclosure of Invention

The present invention intends to solve the problems involved in the prior art described hereinabove. More specifically, it is an object of the present invention to solve such problems as reduction in the heat-exchanging efficiency due to the condensed water, scattering water drops, and generation of foreign odor, and problems in the production process, and the like, and to provide a hydrophilization agent, a hydrophilization liquid free of chromium, which can impart improved hydrophilic property and corrosion resistance, and such hydrophilization method, a metallic material and a heat exchanger,

The present inventors gave extensive considerations to a solution of the above-described problems and discovered that these problems can be solved by means of applying on the surface of metallic material a hydrophilization agent which contains a hydrophilic polymer having a particular non-ionic functional group, a water-soluble polymer having a particular ionic functional group, a vanadium compound, and a compound having at least one element selected from Zr, Ti, Si. Thus, the present invention was completed.

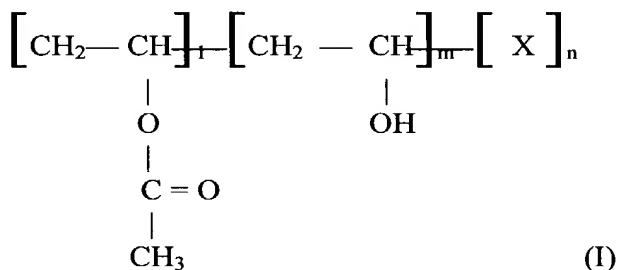
Namely, the hydrophilization agent of metallic material according to the present first invention characterized in that it contains:

- (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;
- (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;
- (C) a vanadium compound; and,

(D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

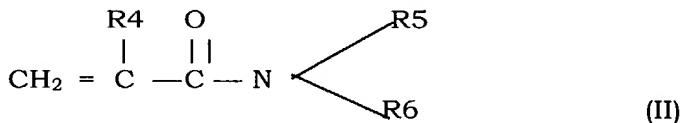
The present invention is described hereinafter in detail.

Preferably, the hydrophilic polymer having said a non-ionic functional group (A) in said hydrophilization agent is at least one selected from the polyvinyl alcohol polymer expressed by the following general formula (I) and a reaction product of the polyvinyl alcohol polymer expressed by the following general formula (I) and a diketene.



In the above formula (I), X indicates a copolymerizing unit other than vinyl acetate and vinyl alcohol, and l, m and n indicate the copolymerizing number of the moles of a vinyl acetate copolymerizing unit, a vinyl alcohol polymerizing unit, and the copolymerizing unit X, respectively, $l+m+n = 100$, and l and n may be zero.

Preferably, the hydrophilic polymer having a non-ionic functional group (A) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following general formula (II).



R4 indicates a hydrogen atom or CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 - C4, a benzyl group, or a hydroxyalkyl group of C1 - C3.

At least one additive selected from the group consisting of (E) an anti-bacteria/mildew agent, an organic crosslinking agent and a surfactant is preferably contained in addition to the above-mentioned compositions (A) - (D).

Preferably, in the treatment agent according to the present invention, relative to 100 parts by weight of the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements are blended in the weight proportions.

A hydrophilization liquid according to the present second invention is related

to the above-described treatment agent which is applied to form a hydrophilic film on the surface of metallic material and is characterized in that it contains from 0.05 to 50g/L of the hydrophilic copolymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the hydrophilic polymer having an ionic functional group (B) as a solid matter, from 0.05 to 10 g/L of the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of a compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements.

A hydrophilization method of metallic material according to the present third invention is characterized in that the hydrophilization agent of metallic material set forth in any one of claims 1 through 5 is deposited on the surface of the metallic material and is dried to form a hydrophilic film having improved corrosion resistance.

The present fourth invention relates to a metallic material, on which surface a hydrophilic film is formed by means of depositing the hydrophilization agent on the surface of the metallic material and drying the same. The present fifth invention relates to a heat exchanger with a hydrophilic film formed as well.

The contents of the present invention are described in detail hereinunder in detail. First, the hydrophilization agent of the first invention is described.

Embodiments of Invention

Preferably, the hydrophilic polymer having the non-ionic functional group and used in the present invention as the first component contains at least one of: (A-1) which is the polyvinyl alcohol polymer expressed by the above-mentioned general formula (I), and a reaction product of the polyvinyl alcohol polymer and diketene; (A-2) which is a co-condensed polymer of at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following above-mentioned general formula (II), and polyethylene oxide, polyethylene glycoldiamine, adipic acid and ϵ -caplactum.

A partially sponified product and completely sponified product of polyvinyl acetate in the first component (A-1), as well as a partially sponified product and completely sponified product of a copolymer of vinyl acetate and another monomer are included in the first component (A-1). A comonomer, which is copolymerized with the vinyl acetate, is not particularly limited but the following can be listed: acrylic acid, methacrylic acid, itaconic acid, maleic acid, or their salts as the anionic comonomer; styrene, acrylonitrile, vinyl ether, (meth)acrylamide, N-methylol (meth)acrylamide, methyl (meth)acrylate, hydroxyethyl (meth)acrylate, vinyl pyrrolidone, acryloyl morpholine, and vinyl acetate as the non-ionic monomer; and aminoethyl (meth)acrylate, vinylimidazole, and N, N-dimethyl diallylamine as the cationic comonomer.

In the above formula (I), X indicates a polymerizing unit other than vinyl acetate and vinyl alcohol; l, m and n indicate the co-polymerizing number of the moles of a vinyl-acetate polymerizing unit, a vinyl-alcohol unit, and the co-polymerizing unit, respectively. The copolymerizing mole ratio ($n/(l+m+n)$) of the copolymerizing unit (X) is preferably from 0 to 0.4 and is more preferably from 0 to 0.3. In addition, the copolymerizing mole ratio ($l/(l+m+n)$) of the vinyl acetate polymerizing unit is preferably from 0 to 0.2 and is more preferably from 0 to 0.1 in the polyvinyl alcohol polymer of the general formula (I). When these co polymerizing ratios are excessively large, the water solubility of the resultant polyvinyl alcohol compound may be lowered to an unsatisfactory level. The range of the mole ratio ($m/(l+m+n)$) of the vinylalcohol polymerizing unit is determined by the above-mentioned two mole ratios.

Next, the first component (A-2) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the general formula (II) mentioned above.

Here, in the above-mentioned general formula (II), R4 indicates a hydrogen atom or a CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 - C4, a benzil group, or a hydroxyalkyl group of C1 - C3. One polymerized product of acryamide compound (monomer (a-a)) and a co-polymerized product of two or more of acryamide compounds (monomer (a-a)), as well as a copolymer of one or more of an acryamide compound (monomer (a-a)) according to the general formula (II) and one or more other comonomer (a-b) are included in the general formula (II). The comonomer (a-b) used here is selected from anionic, non-ionic and cationic addition-polymerizing monomers which are polymerizable with the acrylamide monomers (a-a). Such comonomer (a-b) can be selected, for example, from anionic unsaturated monomers such as (meth)acrylic acid, itaconic acid, maleic acid, vinyl sulfonic acid, styrene sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonate acrylamide, 2-acrylamide-2-methylpropane-sulfonate, acid-phosphooxyethyl methacrylate, or their salt, non-ionic unsaturated monomers such as (meth)acryl amide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylate, vinyl pyrrolidone, acryloyl morpholine, polyoxyethylene glycolacrylate, and polyoxyethylene glycolacrylate alkylphenylether, and cationic unsaturated monomers such as aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl-aminoethyl(meth)acrylate, N-hydroxymethyl-aminoethyl methacrylate, vinyl imidazole, vinyl pyridine, N, N diallyl amine, and N, N-diallyl-N, N-dimethyl ammonium chloride. In addition, the comonomer (a-b) may be selected from such addition-polymerizable monomers not having high hydrophilic property as styrene, acrylonitrile, vinylether, acrylester group and vinylacetate. In this case, the copolymerizing ratio of the comonomer used is selected to maintain the water solubility of the resultant copolymer to the desired level.

One polymer and two or more copolymers of the above-mentioned acrylamide monomer (a-a) mentioned above, as well as a copolymer of one or more of the acrylamide monomer (a-a) and the comonomer (a-b) may be subjected to a post-treatment or post-reaction to change their structure. The so-treated copolymer may be used as the hydrophilic polymer having a non-ionic functional group (A), for example as follows: a reaction product, which is obtained by bringing an amine group and formalin into reaction with the amide group, and which is converted to an aminoalkyl group (Mannich reaction); the amide group, which is converted to an amino group by a decarboxylation reaction, causing alkyl and bromine to react with the amide group (Hofmann reaction); the side-chain ester group, which is converted to an amino group by an ester-amide interchange reaction, causing the alkyldiamine to react with the side-chain ester group; and a quaterized amino group.

The hydrophilic polymer having an ionic functional group (B) and constituting the second component used in the inventive hydrophilization agent has at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group.

The hydrophilic polymer having an ionic functional group (B) of the second group is largely classified into (B-1), a polymer not having a cationic group but having at least one ionic functional group selected from the anionic group which consists of a sulfonic acid group, a phosphonic acid group and a carboxyl group, and (B-2), a polymer not having an anionic group and having at least one member

selected from the group of a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group. In the second component used in the present invention, it is desirable that the above-mentioned anionic hydrophilic polymer (B-1) and the above-mentioned cationic hydrophilic polymer (B-2) are not used in combination.

The anionic monomer (b-1), which forms the anionic hydrophilic polymer not having a cationic group (B-1), can be selected from vinyl sulfonate, styrene sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, N-methylene sulfonic acrylamide, 2-acrylamide-2-methyl propane sulfonate, vinylphenol sulfonate, acid phosphoxy ethylmethacrylate and their salts.

The cationic monomer (b-2), which forms the cationic hydrophilic polymer (B-2) can be selected from aminoethyl (meth)acrylate, N, N-dimethyl-aminoethyl acrylate, N-hydroxypropyl aminoethyl(meth)acrylate, N-hydroxymethyl aminoethyl methacrylate, vinylimidazole, vinylpyridine, N, N diallylamine, and N, N-diallyl-N, N-dimethylammonium chloride. Each of these monomers (b-1) and (b-2) may form a hydrophilic homopolymer and may be copolymerized with a polymerizable comonomer to form a hydrophilic polymer. The above-mentioned comonomer includes the above-mentioned monomer (b-1) and (b-2) as well as other monomers (b-3), for example, acrylamide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylate, vinylpyrrolidone, acryloyl morpholine, polyethylene glycol acrylate alkylphenylether, acrylic acid, methacrylic acid, itaconic acid, maleic acid, their salts, styrene, acrylonitrile, vinyl ether, acryl ester group, vinyl acetate and the like. The comonomer may be a low-hydrophilic monomer such as styrene, acrylonitrile, vinyl ether and (meth)acryl esters. When such low hydrophilic monomer is used, its co-polymerizing ratio is set so as not to impair the desired water solubility of the resultant copolymer.

The vanadium compound (C) which is the third component used in the hydrophilization agent of the present invention, is an inorganic or organic compound which contains vanadium having a possible valence. Metavanadic acid, vanadic acid and its salt (sodium, potassium, ammonium), vanadium oxide such as vanadium pentoxide, halides such as vanadium pentachloride and vanadium pentafluoride, organic vanadium compounds such as vanadic acetylacetate and vanadyl acetyl acetate, vanadyl sulfate, vanadium sulfate, vanadium nitrate, vanadium phosphate, vanadium acetate, and vanadium biphosphate can be listed.

A reducing agent may be used in combination with the above-mentioned vanadium compound to partially or completely reduce the vanadium compound, as a means for incorporating it into the hydrophilization agent according to the present invention. The reduced vanadium compound is thus included in the hydrophilization agent.

The fourth component contained in the hydrophilization agent of the present invention is a compound having at least one element selected from the group consisting of Zr, Ti, Si. This is a water-soluble or water-dispersing compound. Preferably, for example, zirconium compounds such as zirconium- ammonium carbonate, zirconyl nitrate, zirconyl sulfate, zirconyl nitrate, zirconium fluoric acid, and their salts, a titanium compound such as diisopropoxy titanium- bis acetylacetone, fluoro titanate acid and their salts, silicofluoric acid and its salt, and alkali silicate are used as the compound.

An anti-bacteria agent and/or anti-mildew agent as the fifth component may be added into the hydrophilization agent according to the present invention so as to suppress the putrefaction odor due to propagation of mildew, bacteria and yeast, provided that the effects of the present invention are not impeded by the fifth component. Desirably, the anti-bacteria/mildew agent usable in the present

invention is such that it can resist, during the drying step after applying the inventive treatment agent, the heating for removing the water, which is a solvent of the treatment agent. That is, the anti-bacteria/mildew agent desirably does not have a decomposition temperature at 100 °C or less.

5 An anti-bacteria and/or mildew agent, which is added in the hydrophilization agent according to the present invention, can be selected, for example, from 5-chloro-2methyl-4-isothiazoline-3-on, 2-methyl-4-isothiazoline-3-on, 2-(4-thiocyano-methylthio)benzothiazole, 2, 2-dibromo-3-nitrilopropion amide, sodiummethylene bis(dithiocarbamate), sodium-2-pyridinethiol-1-oxide, zinc-2-
10 pyridinethiol-1-oxide, 2, 2'- dithiobis (pyridine-1-oxide), 2, 4, 5, 6-tetrachloro isophthalonitrile, 2-methylcarbonyl aminobenzimidazole, 2, 3, 5, 6-tetrachloro-4-(methylsulfonyl)-pyridine, 2-(4-thiazolyl) benzimidazole, N-(fluoro dichloromethyl thio) sulfamide, p-chloro-m-xyleneol, dehydroacetic acid, o-phenyl phenol, 1, 2-benzisothiazoline barium, diiodemethyl-p-toulenesulfone, 2-n-octyl-4-
15 isothiazoline-3-on, and 10, 10' oxybisphenoxyarsine and the like.

The addition amount of the anti-bacteria and mildew agent is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore, preferably from 0.5 to 30% by weight based on the total of the first component (A) and the second component (B).

20 In the present invention, a three-dimensional structure can be formed by utilizing a functional group of the A component, thereby enhancing the water resistance of the film. A water-soluble cross-linking agent can be used for such purpose.

25 The cross-linking agent, which is included in the hydrophilization agent according to the present invention, can be selected from water-soluble blocked polyisocyanate, polymethylol, polyglycidyl, polyaziridile compound, and an aldehyde group. That is, an organic cross-linking agent can be selected from block polyisocyanate bisulfate, methylol melamine, methylol urea, methylolized polyacrylamide, polyethylene glycol glycidyl ether, diaziridilated polyethylene oxide, glyoxal, furfural and the like.

30 The addition amount of the cross-linking agent is preferably from 0.1 to 70% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B). When the addition amount is less than 0.1% by weight, the cross-linking effect is insufficient. When the addition amount exceeds
35 70% by weight, the film becomes too hard and brittle and is not preferable in terms of formability and adhesiveness.

If necessary to further improve the lubrication property of the film formed by using the hydrophilization agent according to the present invention, or to improve the coating performance of the agent, a surfactant may be added. The surfactant
40 used for this purpose may be any one of the anionic, cationic, non-ionic or amphoteric surfactant. However, it is not preferable to use a surfactant having an ionic property opposite to that of the polymer of the components (A) and (B) used in combination with the surfactant, since the stability of the treating liquid may be impeded.

45 The following are examples of surfactant capable of adding into the hydrophilization agent according to the present invention: non-ionic surfactant such as polyoxy-ethylene alkylether, e.g., polyoxyethylene laurylether and polyoxyethylene stearyllether, polyoxyethylene alkylphenylether, e.g., polyoxyethylene nonylphenylether, sorbitan fatty ester, e.g., a block polymer of
50 oxyethylene and oxypropylene (Pluronic), sorbitan monolaurate and sorbitan monostearate, fatty ester of polyoxyethylene, e.g., polyoxyethylene laurate, polyoxyethylene stearate, and polyoxyethylene oleate, glycerin fatty ester, and polyoxethylene propylene glycol alkyl phenol ether; anionic surfactant such as

fatty salt, e.g., sodium laurate, sodium stearate and sodium oleate, alkyl sulfate, e.g., sodium dodecylsulfate, alkylsulfosuccinate, dialkylsulfosuccinate, alkenylsulfosuccinate and polyoxyethylene alkyl sulfate; cationic surfactant such as alkylamine salt, e.g., stearylamine acetate, quaternary ammonium salt, e.g., stearyltrimethyl ammonium, alkylbetaine, e.g., lauryl betaine, and amine oxide; and, amphoteric surfactant such as aminopropionate and alkyl dimethyl betaine. In addition, the fluorine-based surfactant and the silicon-based surfactant can be used. The addition amount of the surfactant used is preferably from 0.1 to 70% by weight, more preferably from 0.3 to 50% by weight; furthermore preferably from 0.5 to 30% by weight based on 100 parts by weight of the total weight of the first component (A) and the second component (B).

In the hydrophilization agent according to the present invention, it is preferred that, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), from 0.1 to 1000 parts by weight of the second component, i.e., the hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements, are blended in the weight proportions. More preferably, relative to 100 parts by weight of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A), the second component, i.e., the hydrophilic polymer having an ionic functional group (B) is from 1 to 100 parts by weight, the third component, i.e., the vanadium compound (C) is from 1 to 100 parts by weight in terms of vanadium ions, and the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si is from 1 to 100 parts by weight in terms of the elements.

The hydrophilization liquid according to the present invention preferably contains from 0.05 to 50g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.05 to 10 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements. More preferable ranges of the concentrations are: from 0.5 to 10g/L of the first component, i.e., the hydrophilic polymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.5 to 10g/L of the second component, i.e., the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.5 to 5 g/L of the third component, i.e., the vanadium compound (C) in terms of vanadium ions, and from 0.5 to 5 g/L of the fourth component, i.e., the compound (D) having at least one element selected from the group consisting of Zr, Ti, Si in terms of the elements.

The solvent of the hydrophilization agent according to the present invention is mainly composed of water. The combination of water and a water-soluble solvent such as alcohol, ketone, cellosolve and the like in order to adjust the drying speed, to improve the conditions of the coated film, or to enhance the solubility of the components presents no problems. In addition, one or more of a rust preventive, a leveling agent, filler, a coloring agent, an anti-foaming agent and the like may be added into the hydrophilization agent according to the present invention in a range not impairing the gist of the present invention and the film performance.

The hydrophilization agent of the present invention is used as is, or is used

as the surface-treatment liquid, in which the agent is diluted with water. The concentration and the viscosity of the treatment liquid are adjusted appropriately to meet the application method to be employed, the desired film thickness and the like. Preferably, the thickness of the film after drying is from 0.05 to 5 μm , more preferably from 0.1 to 2 μm . When the film thickness is less than 0.05 μm , it is difficult to impart satisfactory hydrophilic property. When the film thickness exceeds 5 μm , there is a possibility that the heat conductivity is inappropriately lowered.

The surface of metallic material to be surface-treated by the present invention is preferably pre-treated by chemical conversion and the like for the purpose of enhancing the corrosion resistance and the like. A chemical conversion treatment agent, which is based on zirconium phosphate, titanium phosphate, vanadium and the like, can be listed as the pre-treatment agent which can enhance the corrosion resistance.

In the hydrophilization method according to the present invention, the surface of the metallic material is degreased, and if necessary, pre-surface treated; subsequently, the hydrophilization agent is deposited on the surface of the metallic material and is then heated and dried to form a film. The application method of the aqueous treatment agent is not particularly limited, and such methods as dipping, spraying, brushing, roll-coating, flow-coating and the like can be used.

The drying method after application of the hydrophilic treatment agent is not particularly limited. Usually, a hot-blast drying oven and the like are used to dry at a temperature of from 80 to 300°C, more preferably from 100 to 250°C to form a film.

Best Mode for Carrying Out Invention

The present invention is further explained with reference to the following examples, which however do not limit the present invention.

Examples 1 - 9 and Comparative Examples 1 - 5

In each of Examples 1 - 9 and Comparative Examples 1 - 5, the metallic material was subjected to the following pre-treatment. After the pre-treatment, the following hydrophilization agents were used to prepare the surface-treated metallic materials. The tests described below were carried out.

(1) Pre-treatments

The pre-treatment by the methods shown in Table 1 and Table 2 was applied to various metallic materials.

Pre-treatment (A)

Al-Mn based alloy sheets (JIS-A3004, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name - Fine Cleaner 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned Al-Mn based alloy sheets were dipped for 60 seconds in the aqueous solution, which was held at 40°C and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name - N405, a product of Nihon Parkerizing Co., Ltd.), followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate film (from 30 to 40 mg/m² in terms of the depositing amount of zirconium) was formed on the surface of the aluminum sheets.

Pre-treatment (B)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet

thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name - Fine Cleaner 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. The surface-cleaned aluminum sheets were dipped for 60 seconds in the aqueous solution, which was held at 50°C and contained 40g/L of a zirconium-phosphate treating liquid (registered trade name - N405, a product of Nihon Parkerizing Co., Ltd.) , followed by washing with potable water. Drying was carried out at 80°C for 30 seconds. A zirconium phosphate film (from 25 to 35 mg/m² in terms of the depositing amount of zirconium) was formed on the surface of the aluminum sheets.

Pre-treatment (C)

Aluminum sheets (JIS-A1100, 70mm×150mm, 0.12mm of sheet thickness) were dipped for 90 seconds in an aqueous solution, which was held at 60°C and contained 30g/L of a weakly alkaline detergent agent (registered trade name - Fine Cleaner 315, a product of Nihon Parkerizing Co., Ltd.) so as to remove contaminating matter on the surface, such as oil. The sheets were then washed with potable water. Drying was carried out at 80°C for 30 seconds.

(2) Hydrophilization Treatment

The hydrophilization treatment by the following methods was applied to the metallic material, which had been pre-conditioned as described above. The treatment methods used are shown in Fig. 1 (Table 1) and Fig. 2 (Table 2).

Hydrophilization Method (A)

The hydrophilization liquid was adjusted to have 3% of total nonvolatile matter content. Immersion in the hydrophilization liquid was carried out at room temperature for 10 seconds. Setting was carried out for approximately 20 seconds, and the heating and drying were then carried out at 160°C for 5 minutes. Incidentally, the target amount of the hydrophilic film was from 0.3 to 0.5 g/m².

Hydrophilization Method (B)

The hydrophilization liquid was adjusted to have 7% of total nonvolatile matter content. Bar-coating was carried out using a bar-coater No. 3 (the target value of wet application amount was 4.5mL/m²). The heating and drying were then carried out at 200°C for 10 seconds.

(3) Components of Hydrophilization Agent

The treatment agents were adjusted using the following components and additives. The composition of the treatment liquid is shown in Table 1 and Table 2.

(A) Components of Hydrophilic Polymer having a Non-ionic Functional Group

- 1 Polyvinyl alcohol (saponification degree - 90 mol %, molecular-weight - 100,000)
- 2 5 mol % - diketene-treated polyvinyl alcohol (saponification degree - 90 mol %, molecular-weight - 50,000)
- 3 acrylamide polymer (molecular weight - 70,000)
- 4 acrylamide/acrylic acid = 50/50 (molecular weight = 50,000)

(B) Components of Hydrophilic Polymer having an Ionic Functional Group

Polymer having an Anionic Hydrophilic Functional Group (B-1)

- 1 Copolymer of acrylic acid/sulfoethyl methacrylate (80/20) (Molecular weight - 70,000)
- 2 Copolymer of acrylic acid/sodium vinylsulfonate (60/40) (Molecular weight - 30,000)
- 3 Sodium polystyrene sulfonate (molecular weight - 50,000)

Polymer having a Cationic Hydrophilic Functional Group (B-2)

4 Polydimethyl diallyl ammonium chloride (molecular weight - 20,000)

5 Block polymer of adipic acid, amino ethyl piperazine and - caprolactum (molecular weight - 10,000)

(C) Vanadium Compound

1 Sodium vanadate

2 Ammonium metavanadate

(D) Compound having at least one element selected from the group consisting of Zr, Ti, Si

1 Titanium fluoroammonium

2 Fluoro zirconate

3 Ammonium zirconium carbonate

(E) Additive

Anti bacteria Agent

1 Zinc-2-pyridinethiol-1-oxide

2 2-n-octyl-4-isothizaoline-3-on

3 2,2-dibromo-3-nitrylopropylamide

(Organic cross-linking agent)

4 Glyoxal

5 Polyethylene glycol-polyisocyanate prepolymer, block polymerized by sodium sulfite (isocyanate content: 5.0 -5.5)

(Surfactant)

6 Discol R-612, product of Daiichi Industry Pharmacy Co., Ltd. (non-ionic surfactant)

(4) Test and Evaluation

The following tests and evaluation were carried out for the treatment sheets, which were prepared in each of Examples 1 - 9 and Comparative Examples 1 - 5. The test results are shown in Table 3 and Table 4.

(Hydrophilic Property)

The treated materials for the test were immersed in flowing water at room temperature for 8 hours, followed by drying at 80°C for 16 hours, as one cycle of the treatment. Five cycles of treatment were carried out. The contact angle of water on the surface of the resultant test samples was measured by using an image-processing type contact-angle meter CA-X(Product of Kyowa Interface Chemistry Co., Ltd.)

(Prevention of Foreign Odor Generation)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80°C for 1 hour and exposure to the water vapor of boiled de-ionized water for 1 second. The foreign odor was quickly smelled and evaluated.

Evaluation Criterion

○: No appreciable foreign odor

△: Somewhat appreciable foreign odor

×: Evidently appreciable foreign odor

(Corrosion Resistance)

The salt-spray test based on JIS-Z-2371 was carried out. After spraying for 240 hours, the state of white rust generation on the samples was evaluated.

Evaluation Criterion

: No generation of white rust

○: Less than 10% of generated area of white-rust

△: From 10 to less than 30% of generated area of white rust

×: 30% or more of generated area of white rust

(Anti-bacteria Property)

The treated materials for the test were immersed in flowing water at room temperature for 72 hours, followed by drying at 80°C for 1 hour. The so-treated materials were cut into 3 cm squares. Nutrient Broth and a 1 : 1 mixture liquid of heptone and glucose were used as the nutrient source of bacteria and mildew, respectively. The nutrient source was deposited on the surface of the test pieces, and a mixed suspension liquid of the following bacteria was sprayed on the deposited nutrient source. Culture was carried out at $30 \pm 2^\circ\text{C}$ for 14 days. The bacteria was extracted from the post-cultured treated sheets into the bacteria-controlled water. The number of bacteria in the bacteria-controlled water was measured by using a dilution culture method.

Evaluation Criterion

○: Less than $10^2/\text{m}^2$ of the bacteria number

△: Not less than $10^2/\text{m}^2$ and less than $10^5/\text{m}^2$ of the bacteria

×: Not less than $10^5/\text{m}^2$ of the bacteria number

Bacteria Used

Bacteria: *Escherichia coli*, *Bacillus subtilis*

Pseudomonas aeruginosa

Mildew: *Aspergillus niger*, *Penicillium citrinum*

Cladosporium cladosporioides

As is apparent from the results of Table 3 and Table 4, the treated materials obtained in Examples 1 - 9, in which the inventive hydrophilization agent and treatment method were used, exhibit improved hydrophilic property even under the durability test conditions and improved property for prevention of foreign odor. The corrosion resistance test also revealed improved resistance. Contrary to these results, the durability of the film was poor, and the preventive property of foreign odor and the corrosion resistance failed in Comparative Examples 1, 4, in which no hydrophilic polymer component having a non-ionic functional group (A) was used. The hydrophilic property of the resultant film was unsatisfactory in Comparative Example 2, in which no polymer component having an ionic functional group (B) was used. The corrosion resistance of the resultant film was poor in Comparative Example 3, in which no vanadium-compound component was used, and in Comparative Example 5, in which no compound containing at least one element selected from the group consisting of Zr, Ti, Si (D) was used.

Industrial Applicability

The hydrophilization agent and the treatment method of the present invention, when applied to the metallic material, particularly the aluminum-containing metallic material, can form on the surface of said metallic material a non-chrome film, which exhibits improved corrosion resistance, hydrophilic property and preventive property of foreign odor for a prolonged period of time, without using a chromic acid film for pre-conditioning.

Table 1 Composition of Hydrophilization Agent of Examples

Exam- ples	Pre- adjust- ing Method	Treat- ment Method	Hydrophilization						
			Composition of Treatment Liquid (weight parts)						
			(A)	(B)	(C)	(D)	(E)		
							Anti- mildew Agent	Cross- linking Agent	Active Agent
1	A	A	① (50)	① (25)	① (4)	① (8)	① (3)	④ (10)	
2	B	A	① (25)	② (40)	① (25)	③ (10)	③ (3)	⑤ (5)	⑥ (2)
3	C	A	② (40)	① (20)	② (15)	② (15)	② (5)	⑤ (5)	
4	B	B	② (40)	③ (30)	① (12)	② (8)		④ (6)	
5	B	A	③ (35)	④ (35)	② (10)	② (10)	② (3)	④ (5)	⑥ (2)
6	A	A	③ (50)	⑤ (20)	② (10)	① (5)	① (5)	④ (10)	
7	C	A	④ (20)	① (25)	② (25)	① (18)	③ (4)	④ (8)	
8	B	A	④ (30)	③ (35)	① (15)	② (8)	① (3)		
9	A	A	① (20)	② (20)	② (10)	④ (5)	③ (3)		⑥ (2)

Table 2 Composition of Hydrophilization Agent of Comparative Examples

Comparative Examples	Pre-adjusting Method	Treatment Method	Hydrophilization						
			Composition of Treatment Liquid (weight parts)						
			(A)	(B)	(C)	(D)	(E)		
1	A	A	—	① (25)	① (4)	① (8)	① (3)	④ (10)	
2	B	A	① (25)	② —	① (25)	③ (10)	③ (3)	⑤ (5)	⑥ (2)
3	B	A	③ (35)	④ (35)	② —	② (10)	② (3)	④ (5)	⑥ (2)
4	A	A	③ —	⑤ (20)	② (10)	① (5)	① (5)	④ (10)	
5	B	A	④ (30)	③ (35)	① (15)	② —	① (3)	④ (9)	

Table 3 Test Result of Examples

Examples	Test Result				
	Hydrophilic Property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	20-24	○	◎	○
2	<5	12-18	○	◎	○
3	<5	19-25	○	○	○
4	<5	16-21	○	◎	×
5	<5	14-18	○	◎	○
6	<5	22-25	○	◎	○
7	<5	20-25	○	○	○
8	<5	23-26	○	◎	○
9	<5	18-20	○	○	○

Table 4 Test Result of Comparative Examples

Comparative Examples	Test Result				
	Hydrophilic property		Generation of Foreign Odor	Corrosion Resistance	Resistant to Bacteria
	Initial	After Cycles			
1	<5	30-38	×	△	×
2	20-25	35-48	○	◎	○
3	<5	14-20	○	×	○
4	<5	32-39	×	△	×
5	<5	21-25	○	×	○

Claims

1. A hydrophilization agent of metallic material, characterized in that it contains:

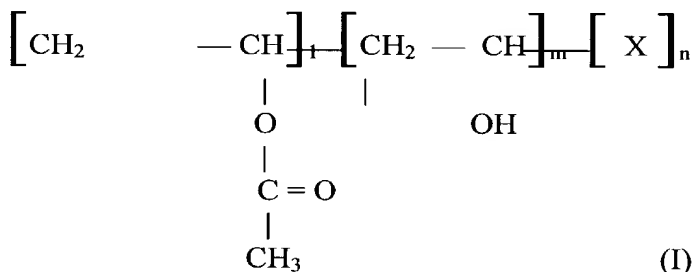
(A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;

(B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;

(C) a vanadium compound;

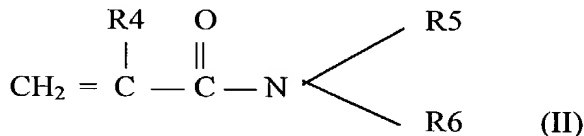
(D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

2. A hydrophilization agent according to claim 1, wherein said component (A) is at least one selected from the polyvinyl alcohol polymer expressed by the following general formula (I) and a reaction product of the polyvinyl alcohol polymer expressed by the following general formula (I) and a diketene,



in the above formula (I), X indicates a copolymerizing unit other than vinyl acetate and vinyl alcohol, and l, m and n indicate the copolymerizing number of the moles of a vinyl acetate copolymerizing unit, a vinyl-alcohol polymerizing unit, and the co polymerizing unit X, respectively, and l and n may be zero.

3. A hydrophilization agent according to claim 1, wherein said component (A) is at least one acrylamide polymer selected from a water-soluble polymer and a water-soluble copolymer of an acrylamide compound expressed by the following general formula (II),



R4 indicates a hydrogen atom or a CH₃ group, and R5 and R6 indicate, each independently of the other, a hydrogen atom, an alkyl group of C1 - C4, a benzyl group, or a hydroxyalkyl group of C1 - C3.

4. A hydrophilization agent according to any one of claims 1 through 3, further containing at least one additive selected from the group consisting of (E) an anti-bacteria/mildew agent, an organic crosslinking agent and a surfactant.

5. A hydrophilization agent according to any one of claims 1 through 4, wherein relative to 100 parts by weight of said hydrophilic polymer having a non-

ionic functional group (A), from 0.1 to 1000 parts by weight of said hydrophilic polymer having an ionic functional group (B), from 0.1 to 200 parts by weight of said vanadium compound (C) in terms of vanadium ions, and from 0.1 to 200 parts by weight of a compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements are blended in the weight proportions.

6. A hydrophilization liquid of metallic material, characterized in that it contains from 0.05 to 50g/L of the hydrophilic copolymer having a non-ionic functional group (A) as a nonvolatile matter, from 0.05 to 50g/L of the hydrophilic polymer having an ionic functional group (B) as a nonvolatile matter, from 0.05 to 10 g/L of the vanadium compound (C) in terms of vanadium ions, and from 0.05 to 10 g/L of the compound having at least one element selected from the group consisting of Zr, Ti, Si (D) in terms of the elements, each set forth in claim 1.

7. A hydrophilization method of metallic material, characterized in that the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 6 is deposited on the surface of the metallic material and is dried to form a hydrophilic film.

8. A metallic material, characterized in that a hydrophilic film is formed on the surface thereof by means of depositing the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 6 on the surface of the metallic material and drying the same.

9. A heat exchanger, characterized in that a hydrophilic film is formed on the surface of a metallic material by means of depositing the hydrophilization agent or hydrophilization liquid of metallic material set forth in any one of claims 1 through 6 on the surface of the metallic material and drying the same.

Abstract

A hydrophilization agent free of chromium can impart to a heat exchanger made of aluminum, improved corrosion resistance and hydrophilic property lasting for long period of time. The hydrophilization agent contains:

- (A) a hydrophilic polymer having at least one non-ionic functional group selected from the group consisting of a primary amide group, a secondary amide group, a tertiary amide group, a hydroxyl group and a polyoxyalkylene group;
- 10 (B) a hydrophilic polymer having at least one ionic functional group selected from the group consisting of a sulfonic acid group, a phosphonic acid group, a carboxyl group, a primary amino group, a secondary amino group, a tertiary amino group and a quaternary ammonium group;
- (C) a vanadium compound; and,
- 15 (D) a compound having at least one element selected from the group consisting of Zr, Ti, Si.

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Number

M 6820 HST/NI PCT/US

First Named
Inventor

Nakada, Kazuya

COMPLETE IF KNOWN

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that

My residence, post office address, and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

HYDROPHILIZING AGENT FOR METALLIC MATERIAL, HYDROPHILIZING FLUID, METHOD OF HYDROPHILIZING, METALLIC MATERIAL, AND HEAT EXCHANGER

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) **10/8/1999** as United States Application Number or PCT InternationalApplication Number **PCT/JP99/05652** and was amended on (MM/DD/YYYY) _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56

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Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed		Certified Copy Attached?	
			YES	NO	YES	NO
10/293656 11/288204	Japan Japan	10/15/1998 10/ 8/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/JP99/05652	10/8/1999	

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As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor					
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